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1988

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ПОЛУЧЕНИЕ И ХАРАКТЕРИСТИКА НЕКОТОРЫХ АКТИВНЫХ ФОРМ MnO_2 ДЛЯ ГАЛВАНИЧЕСКИХ СУХИХ ЭЛЕМЕНТОВ И БАТАРЕЙ (II)

Н. КАЛУ, И. САНДУ, АНИШОАРА БОЛД, И. БЕРДАН и САНДА ИОРДАН

1. Введение

В производстве катодной смеси на базисе высоких марганцевых окисей индустрия галванических сухих элементов и батарей применяет как для солевых систем, так и для щелочных, — искусственный диоксид марганца, полученный электрохимическим путем (ЭДМ) или химическими методами (ХДМ) в чистом виде или в смеси с природным диоксидом марганца (ПДМ), очень активного действия [1].

Методы получения активного марганца, выявленные в ходе нашего исследования [2] ... [5], можно сгруппировать следующим образом :

1. Химические методы с изменением состояния окисления, основанные на следующих процессах: а) окисление ионов Mn (II); б) восстановление ионов MnO_4^- и MnO_4^{2-}; в) термическая обработка некоторых солей Mn (II) и т.д.

2. Методы активизации диоксида марганца из руды химическим или физико-химическим путем, с изменением или без изменения состояния окисления Mn (IV).

В синтезе диоксида марганца особое внимание нужно обратить на условия реакции : природа и концентрация реактантов, pH среды, температура, скорость смешивания, природа и концентрация твердых инертных фаз и т.д., которые влияют на электрохимическую активность продукта. Это обусловлено тем, что данный метод изготовления определяет структуру (алотропное состояние диоксида марганца) и другие физико-химические характеристики.

Химические методы получения активного диоксида марганца представляют некоторые преимущества в сравнении с электрохимическими, как по качеству активного продукта, так и по экономическому признаку ; последние — дешевле.

Отметим следующие характеристики активных форм диоксида марганца, полученного химическим путем, которые определяют его электрохимическую емкость : а) природа различных сосуществующих фаз в конечном продукте, б) природа и концентрация компонентов фаз (Mn (IV), Mn (III), Mn (II), H(I) другие ионы); в) содержание в гигроскопической и химически соединенной воде; г) система кристаллизации (элементарная клетка, число структурных единиц между элементарной клеткой и т.д.) ; д) активная поверхность, порозность и т.д.

В этом смысле, различные активные формы MnO_2, полученные химическим путем, представляют различные твердые растворы с алотропными модификациями, со статическими распределениями и нестоэхиометрическими химическими составами, приблизительные грубые формулы которых, подсказанные Бренетом и сотр. [6] типа :$MnO_{x-y}(OH)_{2y} \cdot nH_2O$ для вариации γ-MnO_2 установлено, что $y = 2—x$, что ведет к формуле : $(MnO_2)_{2y-3}(MnOOH)_{4-2y} \cdot nH_2O$, где y имеет значения между 1,5 ... 2.

Некоторые аспекты по характеристике диоксида марганца могут быть освещены на основе физико-химических методов анализа : химичесий анализ, спектроскопия ИК, спектроскопия лучами X, термогравиметрический анализ, тестами активности и т.д.

В данной работе представлены некоторые данные по получению и характеристике двух активных продуктов диоксида марганца химическим анализом, термической дериватографией в статическом и динамическом режимах, а также спектрографией лучами X. Полученные данные позволили сопоставить физико-структурные свойства с химической и электрохимической активностью активных продуктов.

2. Экспериментальная часть

Для улучшения качества марганцевых окисей со слабой активностью мы выработали, исходя из внутренних ресурсов руд пиролузита, два метода получения MnO_2 высокой активности, с уменьшением, в то же время, содержания окиси железа и двуокиси кремния.

2.1. Получение активных продуктов

Представим получение двух активных продуктов :

а) *Получение продукта 1* [7]. Определенное количество марганцевой руды, заранее смешанное, было растворено в растворе серной кислоты 10...20% с прибавлением при постоянном разбалтывании смеси Na_2MnO_4—$NaMnO_4$, при температуре 90°C, в течении 6 часов. После концентрации раствора продукт был профильтрован и промыт водой до pH=5. После просушки продукт был перевеведен в расплавленную смесь NaOH 45%—Na_2CO_3 35%, при температуре 450°C в течении часа. Na_2MnO_3, который образовался, был тщательно размолот и был обработан раствором азотной кислоты 5 M. Поддерживалась постоянная температура 60°C, а pH $\leqslant$3. Полученная суспенсия была профильтрована, промыта и просушена на воздухе при нормальной температуре.

б) *Получение продукта 2* [8]. Получение продукта *2* из руды окисей марганца слабой активности основывается на целом ряде физико-химических процессов, которые состоят в параллельной обработке двух фракций. Одна фракция обрабатывается расплавленной смесью NaOH—$KClO_3$ и получается $NaMnO_4$. Другая фракция была предварительно нагрета до 700°C для восстановления Mn(IV) до Mn(II) и обработана концентрированной соляной кислотой. В этих условиях получается $MnCl_2$. На втором этапе Na_2MnO_4 в виде щелочного раствора, дабавляется при постоянном помешивании в раствор $MnCl_2$ при pH=1. Во время реакции pH постоянно поддерживался на pH=3,5. Поддерживание постоянного pH осуществлялось с помощью азотной кислоты. Вследствие реакции между ионом MnO_4^{2-} и Mn^{2+} образуется с достаточным коэффициентом двуокись марганца высокоактивная и очень чистая.

Полученный продукт был обработан азотной кислотой 5 M в течении шести часов при температуре 60°C. Полученная суспенсия была промыта дистиллированной водой до полного удаления иона основного раствора, а потом продукт был просушен 2 ... 4 часа при температуре 60°C. После просушки эти две пробы были тщательно размельчаны и пропущены через комплекс вибрирующих сит. Фракция, оставшаяся на сите 0,0042 (стандарт 1 077/1976) была помещена в герметически закрытую ампулу, помещенную в свою очередь в эксикатор с $CaCl_2$ ангидр.

2.2. Химический анализ

Новосинтетизированные продукты содержат марганцевые окиси в различных состояниях окисления, а также вариирующее количество воды для увлажнения и конституции. Содержание марганцевых окисей, которое выражается Mn(IV), Mn(III), Mn(II) в процентах, было установлено с помощью комплексометрических методов, а также методом В о л ь х а р д а и редокс [9], [10].

Для определения содержания H(I), соответствующего слабокислотным группировкам $Mn(\geqslant IV)—O]^{-}H^{+}$, были использованы методы кислота-основание, основывающиеся на прослеживании pH некоторых растворов различных концентраций NaOH или KOH, с прибавлением определенного количества MnO_2-активного.

Химическая активность новосинтетизированных продуктов определялось по стасу 1 314/19-1975, использующего метод Д р о ч м а н я а [11], дополненого гравиметрической составом в MnO_2 для продуктов.

2.3. Термогравиметрический анализ

Термический анализ в статическом режиме, изотермическом было осуществлено с помощью печи, что позволило наблюдать термическое поведение продуктов при температуре от 60°C до 1 000°C. Определения осуществлялись на пробах в контакте с воздухом.

Неизотермический термогравиметрический анализ осуществился с помощью дериватографа МОМ-Будапест, типа Паулик — Паулик —Ердей. Были проанализированы свежеполученные пробы MnO_2, а также пробы сохранившееся определенное количество времени, при различных скоростях нагревания.

2.4. Спектроскопия лучами X

Спектры дифракции лучами X были получены с помощью аппарата типа TYR—M 62, используя радиацию $Fe_{K\alpha}$, $\lambda = 1{,}937$ Å и фильтром марганца. Условия работы : потенциал возбуждения 30 ... 45 кВ, ток 8 ... 10 мА, скорость гониометра 1/2 град. мин$^{-1}$ и скорость перемещения бумаги 600 мм/час. Сравнивая параметры θ_{hkl} и ∂_{hkl}, которые были определены, а также интенсивность дифракционных линий с данными, представленными в Powder Diffraction File-Search Manual Inorganic Compounds, I.C.P.D.S., USA, 1973, и в карточках ASTM были определены кристаллические классы, существующие в продукте. Для установления системы кристаллизации была осуществлена индексации диффракционных линий сравнением значений ∂_{hkl}, которые были установлены экспериментально и теоретическими значениями.

2.5. Плотность активных продуктов

Плотность определялась с помощью пикнометра (25 мл), используя толуен, плотность которого имелась в виду, при 26°C, равна 0,8604 г.см$^{-3}$. Массы были взвешены, когда температура системы была 26° ... 27°C.

2.6. Электрохимическая активность

Электрохимическая активность определялась с помощью установки, образованной из полифункциональной ячейки, введенной в соответсвую-

щую электрическую цепь. Метод основан на измерении напряжения разряда таблеки 0,2 г катодной смеси, образованной из 0,16 г MnO_2 и 0,4 г коллоидной графической массы, в отношении с цинковым анодом с постоянной активной поверхностью, при постоянном токе разряда 0,1 А/г MnO_2.

3. Результаты и обсуждения

Результаты химического анализа по определению процентного содержания Mn(IV), Mn(III), Mn(II), H(I), воды (гигроскопической и конституционной) других катионов даны в таблице 1.

На основе экспериментальных результатов был найден x из MnO_x : $x=1{,}854$ для продукта *1* и $x=1{,}958$ для продукта *2*, что соответствует приблизительным формулам $8\,MnO_2 \cdot 2\,MnO(OH) \cdot 3\,H_2O$, соответственно, $7\,MnO_2 \cdot 1\,MnO(OH) \cdot 3\,H_2O$.

Таблица 1

Данные о составе новосинтетизированных продуктов

Компоненты, [%]	*1*	*2*
Mn(IV)	42,35	49,15
Mn(III)	8,73	8,29
Mn(II)	1,08	0,80
H(I)	0,39	0,38
Na(I)	1,56	1,73
SiO_2	12,93	—
H_2O — конституции	5,22	7,66
O_2 — вычисл. по диф.	28,13	33,18

Данные, полученные измерениями pH в гетерогенной системе : водный раствор NaOH—MnO_2, по содержанию MnO_2 в слабокислотных группировках, представленные в рис. 1, указывают на появление скачка pH в отношении эквивалентности 1 NaOH/1 Mn(IV), а для системы KOH—MnO_2 в отношении эквивалентности 1,6 KOH/1 Mn(IV).

Новосинтетизированные продукты представляют высокую химическую активность, 115 ... 125 мл H_2(I) и 130 ... 140 мл H_2 для продукта *2*, которая может длительно сохраняться.

Химическая активность продуктов зависит и от структуры, а также от содержания в них воды и ионов H(I). Это является мотивировкой наблюдения остаточной активности со специфическими потерями при определенных температурах (рис. 2). Для этой цели продукты были нагреты до различных температур до постоянного веса в течении двух часов. Потом определялась остаточная активность и удельные потери $\Delta G_{уд}$, и установлено, что до 110°C продукты теряют примерно 8% (I) своей активности и 9% (II), что связано с потерей гигроскопической воды. В пределах 110 ... 200°C продукт *1* теряет 35% своей активности, а продукт *2*, 30%, когда теряется физически связанная вода и большая часть конституционной воды. На рис. 2 заметна небольшая вариация остаточной активности и

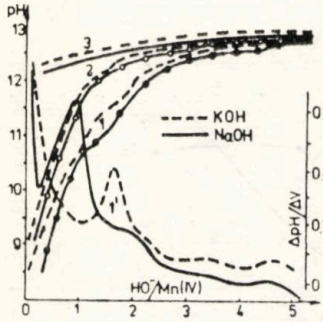

Рис. 1. — Графическое изображение функции pH = f(HO⁻/Mn(IV)): *1* и *1′* — время реакции 144 часа ; *2* — время реакции 24 часа ; *3* — контрольная кривая.

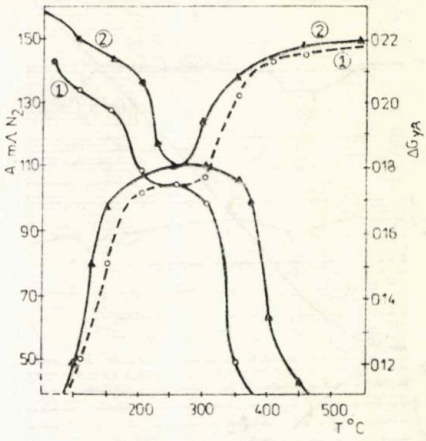

Рис. 2. — Данные удельных потерь и остаточной активности при нагревании в статическом режиме.

удельных потерь в пределах 200°...300°C. Это показывает, что новосинтетизированные продукты представляют относительно высокую стабильность по сравнению с продуктами, полученными электрохимическими методами.

Выше 300°C активность снижается примерно линейно, так что для обоих продуктов при 550°C начальная активность снижается на 90%.

Дериватографические исследования новосинтетизированных продуктов привели к важным выводам касательно поведения этих продуктов в динамическом режиме (рис. 3 и 4).

Влияние скорости нагревания на кинетические параметры n и E было прослежено, регистрируя дериватограммы при различных скоростях нагревания, когда были получены значения E_a=10 Kcal/мол и n=0,5. Эти значения указывают на тот факт, что потеря воды протекает в кинетико-диффузиональном режиме.

Анализом лучами X была получена информация об основном кристаллическом классе системы кристаллизации продуктов и о параметрах элементарной клетки. В таблицах 2 и 3 представлены данные, полученные спектроскопией лучами X. Используя данные таблицы 2 была сделана попытка определения эмпирической формулы активных продуктов, которая проверялась с помощью пикнометрической плотности (4,56 г · см$^{-3}$ для *1* и 4,21 г · см$^{-3}$ для *2*), вычисленной экспериментально и эта плотность сравнивалась с вычисленной теоретически при помощи программы ФОРТРАН IV, адекватной для вычисления параметров элементарной клетки : a_0, $б_0$, $в_0$.

Диффракционный анализ лучами X констатировал, что эти два продукта представили кроме характерных линий орторомбической системы и другие линии, характерные для тетрагональной системы (для *1*) и гек-

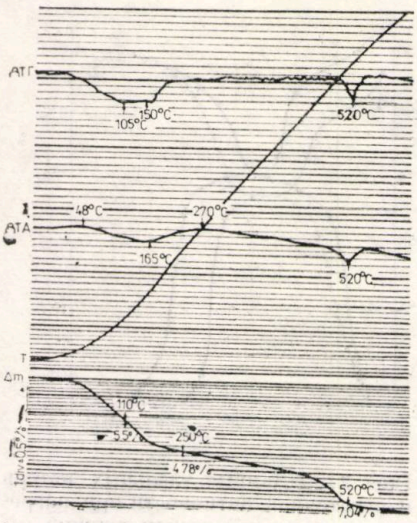

Рис. 3. — Дериватограмма продукта *1*, нагретого предварительно до 60°С: а) количество продуктов 50 мг ; б) чувствительность ДТГ и ДТА : 1/10; в) скорость нагревания 12°С/мин. ; Δm — потеря массы, [%].

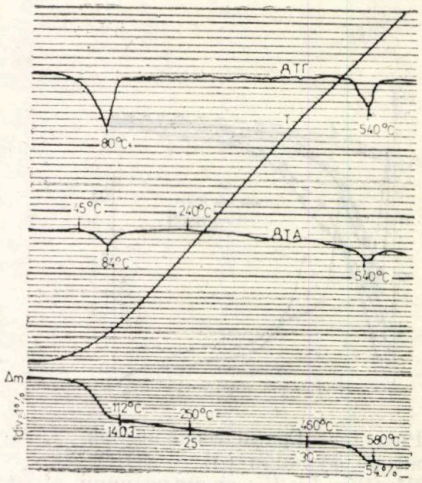

Рис. 4. — Дериватограмма продукта *2*, нагретого предварительно до 60°С: а) количество продуктов 50 мг ; б) чувствительность ДТГ и ДТА : 1/10 ; в) скорость нагревания 12°С/мин. ; Δm — потеря массы, [%].

Таблица 2

Модель дифракции лучами X на порошках MnO_2 типа

Продукт *1*						Продукт *2*					
$\partial_{нагл.}$ Å	I/I_0	Система: орторомб. для MnO_2		Система: тетрагон. для MnO_2		$\partial_{нагл.}$ Å	I/I_0	Система: орторомб. для MnO_2		Система: гексагональн для MnO_2	
		$\partial_{вчсл.}$	hkl	$\partial_{вчсл.}$	hkl			$\partial_{вчсл.}$	hkl	$\partial_{вчсл.}$	hkl
4,85	ос	4,85	020	4,87	200	3,98	obш	4,00	110	3,99	101
3,98	о	3,99	110	—	—	3,26	ос	3,26	120	—	—
3,17	ос	3,17	120	3,15	310	3,09	ос	—	—	3,09	201
2,58	с	2,59	130	2,58	111	2,58	с	2,58	130	2,59	211
2,42	с	2,43	021	2,42	201	2,31	ш	2,32	111	—	—
2,13	ш	2,13	121	2,12	301	2,14	ш	2,14	121	2,13	221
1,63	ш	1,63	221	1,62	600	1,64	ш	1,64	221	1,65	222
1,43	ос	1,43	231	1,42	601	1,43	ос	1,43	231	—	—

о — очень, с — слабый, в — высокий, ш — широкий.

Таблица 3

Эмпирические формулы и структурные параметры активных продуктов 1 и 2

Продукт	Эмпирические формулы: Хим. анализ	Эмпирические формулы: Лучами X	Параметры клетки Объем, [Å]	Плотность, вычисл.*) катион.	Плотность, вычисл.*) анион. пустотами
1	$Mn_{3,3}O_{6,2}\cdot 0{,}95\ H_2O$	$Mn_{3,3}O_{6,5}\cdot 0{,}7\ H_2O$	116,2744	4,456	4,542
2	$Mn_{3,5}O_{6,8}\cdot 1{,}4\ H_2O$	$Mn_{3,5}O_{7,0}\cdot 0{,}8\ H_2O$	123,2453	4,148	4,210

*) для гексагональной системы.

сагональной системы (для *2*). Это доказывает, что продукты содержат кроме преобладающей формы γ-MnO_2 и формы α- и, соответственно, δ-MnO_2.

Электрохимическая активность активных продуктов — 70 мин. для *1* и 82 мин. для *2* (время необходимое для достижения $U_f = 0{,}9$ в), что соответствует примерно активности самых лучших продуктов, полученных химическим путем.

4. Выводы

Новосинтетизированные продукты двумя различными химическими методами, основанными на процессах редокс и процессах кислота — основание, с конечным выделением из растворов HNO_3 5 M при температуре 60°C в течении 5 часов, представляют высокую химическую и электрохимическую активность. Состав продуктов, определенный физико-химическими методами, выявил комплексную структуру и позволил установить связь с поведением в различных химических и электрохимических системах.

Результаты исследования привели к выводу, что активные продукты являются типа γ-MnO_2, которые содержат формы α- и δ-MnO_2.

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PREPARAREA ȘI CARACTERIZAREA UNOR FORME ACTIVE DE DIOXID DE MANGAN PENTRU ELEMENTE ȘI BATERII GALVANICE PRIMARE USCATE

(Rezumat)

Se prezintă unele aspecte privind procesele de sinteză și activare a dioxidului de mangan utilizat în structura sistemelor electrochimice și electronice. Astfel se insistă asupra a două produse active obținute prin metode diferite : unul din produși obținut prin activarea minereurilor bogate în MnO_2 prin topire alcalină ($NaOH + Na_2CO_3$), urmată de descompunerea manganitului de sodiu format cu soluții de acid sulfuric 0,5 N ; celălalt, obținut prin schimbarea stării de oxidare a manganului de la +IV la +II și +VI, a căror interacție conduce la MnO_2-activ de forma $MnO_2 . MnO(OH)_x . nH_2O$, urmată de trecerea în forma H(I) prin dispersie în soluție H_2SO_4 0,5 N.

Produsele nou sintetizate, de tipul γ-MnO_2, impurificate cu formele δ- și α-MnO_2, sînt caracterizate prin metode chimice, fizice și electrochimice. Datorită activității lor electrochimice ridicate, acestea pot fi utilizate drept mase electrochimic-active, pentru elemente și baterii galvanice uscate.

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USE OF THE ION-EXCHANGE MEMBRANES IN THE ANALYTICAL SEPARATION OF Co^{2+} AND Zn^{2+} IONS

BY

FLORICICA MATEI, GH. IONESCU and AL. DUCA

1. Introduction

The use of the ion-exchange membranes (i.e.m.) in electrodialysis for sea-water desalting and for the removing the calcium, manganese, sodium and chlorine ions in different media, is already known [1] ... [11].

The most common membrane stack is an alternate array of cation- and anion-exchange membranes between two electrodes as shown in Fig. 1.

When a sufficiently high external electric potential is applied, the electric current carries cations of the feed stream into the transfer stream through the cation-exchange membrane facing the cathode. But anions are electrically transfered into the transfer stream on the opposite side through the anion-exchange membrane. On the other hand, cations in the transfer stream are rejected by the anion-exchange membrane on the cathode side, and anions by the cation-exchange membrane on the opposite side. Thus, the feed stream is stripped of electrolyte solutes into the two transfer streams around the feed compartment, and the transferred ions remain in the transfer compartment. This electrically driven membrane process is generally called *electrodialysis* in the narrow sence [12].

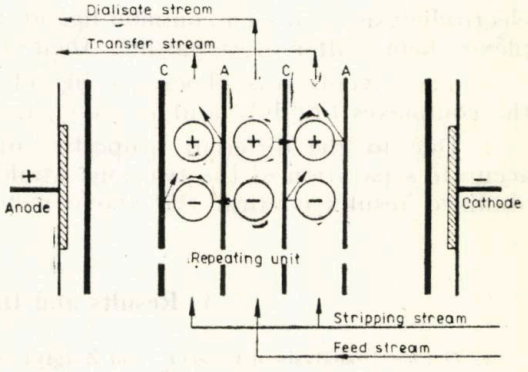

Fig. 1. — The mechanism of the electrodialysis process on ion-exchange membranes

2. Experimental

Taking into account the electrical similarity of the Co^{2+} and Zn^{2+} ions (ionic radius, electric charge, ionic mobility, halfwave potential $E_{1/2}$, etc.) their separation as simple ions by electrodialysis is not expected to be possible [13]. The experimental data confirm this hypothesis (s. Table 1).

The equipment employed is illustrated in Fig. 2.

In order to use the electrodialysis for Co^{2+} and Zn^{2+} separation, the complexating procedure was applied to modify both the charge and the mobility of the ions.

Table 1

Individual Electrodialysis of Co^{2+} and Zn^{2+} without Complexation)*

t, [min.]	10	20	30	40	60	100	120
$10^3.c(Co^{2+})$, [mol/l]	0.068	0.106	0.540	0.670	0.710	0.900	0.970
$10^3.c(Zn^{2+})$, [mol/l]	0.069	0.112	0.570	0.680	0.760	0.910	0.980

*) Ions concentrations in cathodic space : $c_0(Co^{2+})=c_0(Zn^{2+})=1.10^{-3}$ mol/l ; 20°C; current density $d_i=0.65$ A/dm^2 ; KNO_3 10^{-2} mol/l as support electrolyte.

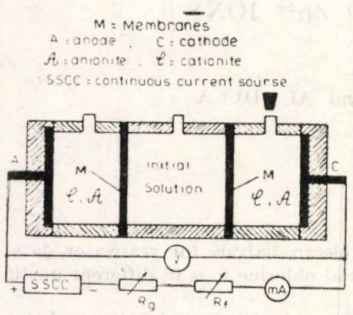

Fig. 2. — The electrodialysis cell.

The chlorine ion is an efficient ligand for Zn^{2+} ion but is not suitable for electrodialysis, because it requires a relatively high concentration (2 mol/l) of it [14]. This ligand has a high mobility and a low redox potential and discharges easily on the anode. This disavantage consists in a possible destruction of the anode, by anodic dissolution.

Besides, the rapid migration of the Cl^- ions leads in short time to the decrease of the Cl^- concentration, below the necessary value for the complex formation (2 mol/l).

For the Co^{2+} and Zn^{2+} separation by electrodialysis we used a common ligand for both ions, the resulting complexes being different, regarding their charge and coordination number.

The glycine was choosen as ligand. This forms with Co^{2+} and Zn^{2+} the complexes $Co(gly)_3^-$ and $Zn(gly)^+$, respectively [15].

Due to the different properties of the complexating products, an accurate separation of the two ions would be expected to be achieved. The obtained results confirm the above mentioned considerations.

3. Results and Discussions

3.1. The Electrodialysis of $Co(gly)_3^-$ and Zn(gly) Complexes from their Individual Solutions

The electrodialysis of the two complexes with ion-exchange membranes (Permaplex A-20, Cl^- form and Permaplex C-10, Na^+ form) was studied initially with respect to $Co(gly)_3^-$ and $Zn(gly)^+$ in individual solutions whose concentrations were of 10^{-3} mol/l for the metallic ion and of 10^{-2} mol/l for the glycine. The temperature of 20°C and 10^{-2} KNO_3 mol/l as support electrolyte were used.

The concentrations were measured spectrophotometrically with Nitroso-R as reagent for Co^{2+} ($\lambda=525$ nm), using a VSU-2P apparatus and by atomic absorption for Zn^{2+} ($\lambda=213.9$ nm), using a SP-90 A Pye-Unicam apparatus in air—acethylene flame [16], [17].

The current density was of 0.86 A/dm^2.

In Fig. 3 the concentration decrease versus time (kinetical curves) for Co^{2+} and Zn^{2+} at the indicated current density is depicted.

The current density choosen is a function of the used concentration. Consequently, we applied the current densities of 0.86 A/dm² and 1.15 A/dm² for concentrations of 10^{-3} mol/l and 5.10^{-4} mol/l orders, respectively. At 2 A/dm² the V_2A anode was dissolved.

The data depicted in Fig. 3 show that Zn^{2+} ions desappear completly in the central compartment after 100 min., while the Co^{2+} ions desappear in proportion of 60%, being completely exhausted after other 100 min. The complexation efficiency in separating of the two ions by electrodialysis is thus evidenced.

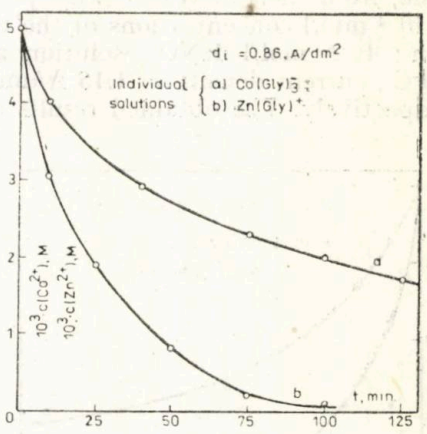

Fig. 3 — The kinetical curves of the $Co(gly)_3^-$ and $Zn(gly)^+$ electrodialysis from individual solutions

By eluting the membranes with 2 mol/l of NaCl solution and after analysis of the eluent, the conclusion was drawn that the $Co(gly)_3^-$ is formed and fixed on the anionic membrane and may pass into the anodic compartment; the $Zn(gly)^+$ is formed too and is fixed on the cationic membrane, as can be seen in Table 2.

Table 2

Eluting of $Co(gly)_3^-$ and $Zn(gly)^+$ Complexes with NaCl

t min.	$10^4.c_0(Co^{2+})$, M (central space)	$10^4.c_0(Zn^{2+})$, M (central space)	$10^4.c_0(Co^{+})$, M (anodic space)	$10^4.c_0(Zn^{2+})$, M (cathodic space)
40	5	5	3.2	3.9
80	5	5	4.4	4.8

$d_i = 1.15$ A/dm²; 20°C; KNO_3 10^{-2} mol/l as support electrolyte; $c_0(NaCl) = 1.10^{-2}$ mol/l; V(central space)/V(anodic space)/V(cathodic space) = 1/1/1; $c_0(gly) = 1.10^{-2}$ mol/l.

Hence, the glycine has the following effects as ligand in the separation process: a) it makes a significant difference between the times of the ion concentration decrease in the central compartment; b) it gives the $Co(gly)_3^-$ and $Zn(gly)^+$ complexes with the two ions and confers opposed charges to the ions.

The shorter fixation time of the $Zn(gly)^+$ complex may be an indication of its formation, being less bulky than the $Co(gly)_3^-$ one and consequently, has a higher mobility.

3.2. The Electrodialysis of $Co(gly)_3^-$ and $Zn(gly)^+$ Complexes from their Common Mixture

The studies on the separation of Co^{2+} and Zn^{2+} complexes with glycine, from their mixtures, were performed under the following conditions : 5.10^{-4} mol/l concentrations of the two ions; 5.10^{-3} mol/l glycine concentration ; 10^{-2} mol/l KNO_3 solution as support electrolyte ; temperature of 20°C ; current density of 1.15 A/dm² and membranes as Cl^- and Na^+ forms, respectively. The obtained results are represented in Fig. 4.

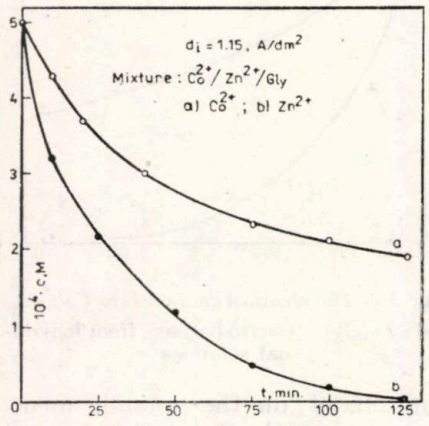

Fig. 4. — The kinetical curves of the $Co(gly)_3^-$ and $Zn(gly)^+$ electrodialysis from their mixture.

The fixation of Co^{2+} and Zn^{2+} is seen to proceed in a longer time (125 min. for Zn^{2+} and 200 min. for Co^{2+}), probably due to the more complex electrostatic interaction in the ions mixture. Zn^{2+} fixes as $Zn(gly)^+$ on the cationic membrane and $Co^{2+}(gly)_3^-$ on the anionic one. The longer time necessary for the appearance of this complexes in cathodic compartment and in anodic one, is probably due to the exchange reactions between the membrane mobile groups (Cl^- and Na^+, respectively) and the $Co(gly)_3^-$ and $Zn(gly)^+$ bulky ions.

This fact may be affirmed since after passing succesively some amounts of solutions containing the two complexes and, hence, after membrane saturation with these ions, the presence of Zn^{2+} and Co^{2+} ions is made evident in a shorter time in greater amounts in the two compartments, as results from the data in Table 3.

Table 3

Eluting and Concentration of $Co(gly)_3^-$ and $Zn(gly)^+$ with NaCl)*

t, [min.]	0	10	20	40	60	80	100	115	130
$10^3.c(Zn^{2+})$, [mol/l] (cathodic space)	0	0.30	0.50	0.78	0.88	0.94	0.97	—	—
$10^3.c(Co^{2+})$, [mol/l] (anodic space)	0	—	0.34	0.62	0.81	0.88	0.94	—	0.98

*) s. § 3.2.

As a consequence of the above described behaviour of the two complexes the electrodialysis technics might be applied in the following directions :

a) Separation and analysis of the Co^{2+} and Zn^{2+} ions in their mixture. The ion-exchange membrane must be initially saturated as Cl^- (anionic membrane) form and as Na^+ form (cationic membrane). For analysis the

complexees fixed on the two membranes are eluted also by electrodialysis, using a NaCl solution of a certain concentration which is maintained constant in the central compartment.

b) Concentration of the two ions from their dilute solutions, namely $Zn(gly)^+$ in the cathodic compartment and $Co(gly)_3^-$ in the anodic one. In this aim the anionic exchange membrane must be initially saturated as $Co(gly)_3^-$ form, while the cationic ones as the $Zn(gly)^+$ form.

As a consequence of these initial conditions of the concentration process, the Co^{2+} and Zn^{2+} ions will pass into the corresponding compartments as complexes formed in the central space of the cell without being retained by the membranes (in other words will substitute equal amounts on the membrane). By using a central compartment of a volume much larger than that of the lateral compartments (anodic and cathodic) or introducing from time to time several portions of dilute solution of the two ions, their concentrations in the lateral compartments may be increased till a desired value.

At the compartment volume ratio of 2.5 (central/anodic, central/cathodic) for the used cell the concentration was performed as follows: 5 portions of 100 cm^3 of solution containing complexes of Zn^{2+} and Co^{2+} with glycine were introduced for obtaining their concentration in the lateral compartments. Each portion in the central space was substituted after checking the ion exhaustion by the described analysis. In the anodic and cathodic compartments a 10^{-2} mol/l KNO_3 solution support was initially introduced, without eliminating their contents which resulted in Zn^{2+} and Co^{2+} ions concentration.

Consequently, by described electrodialysis and complexation procedure the Zn^{2+} and Co^{2+} ions could be separated on the ion-exchange membranes and simultaneously, their concentration in the two lateral compartments may be realised.

4. Conclusions

On the bases of the reported data, the following conclusions may be drawn:

1. Using the electrodialysis technic based on ion-exchange membranes and complexation phenomenon of Co^{2+} and Zn^{2+} ions with glycine, these two ions were separated from their common mixture.

2. Simultaneously, a concentration process of Co^{2+} and Zn^{2+} as complexes with glycine may be realized, namely $Zn(gly)^+$ in the cathodic compartment and $Co(gly)_3^-$ in the anodic one. In this aim the anionic ion-exchange membrane must be initially saturated as $Co(gly)_3^-$ form, while the cationic ones as the $Zn(gly)^+$ one.

3. Besides these problems, a current density influence on separation process of two ions was analysed.

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UTILIZAREA MEMBRANELOR SCHIMBĂTOARE DE IONI ÎN SEPARAREA ANALITICĂ A IONILOR Co^{2+} ŞI Zn^{2+}

(Rezumat)

Utilizînd membrane schimbătoare de ioni, anionice şi cationice (Permaplex A-20 şi Permaplex C-10), se descrie separarea analitică prin electrodializă a ionilor Co^{2+} şi Zn^{2+}, în scopul analizei lor în amestec. Proprietăţi electrochimice sensibil diferite, necesare separării prin metoda propusă, au fost realizate pentru cei doi cationi, prin obţinerea prealabilă a complecşilor lor cu glicocol. În acest mod a fost stabilită o tehnică eficientă de separare a ionilor dintr-un amestec al acestora, după care pot fi analizaţi cantitativ, printr-o metodă adecvată. Ionul Co^{2+} a fost analizat pe cale spectrofotometrică cu reactivul nitro-R ($\lambda = 525$ nm), iar ionul Zn^{2} prin metoda absorbţiei atomice ($\lambda = 213{,}9$ nm) în flacără de aer—acetilenă.

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Cd (II) ACCUMULATION WITH *ESCHERICHIA COLI* AND *SARCINA LUTEA* AS „MICROBIOLOGICAL COLLECTORS"

BY

VIORICA DULMAN and ŞELI ŞFARTZ

1. Introduction

The influence of Cd (II) on bacteria is little studied. From soils contamined with cadmium a bacterium from the genus *Pseudomonas* has been isolated and by incubation it concentrates this ion rapidly. It is assumed that the ion Cd (II) is located both within the cells in combination with the proteins and on the bacterian surface [1].

There has also been isolated from waste waters bacterium *Pseudomonas aeruginosa* that adapts itself to various concentrations of cadmium from waters and the intracelular distribution of this ion has been investigated [2]. There are also other microorganisms that are influenced by or can adapts themselves to the presence of cadmium [3], [4].

It is a well-known fact that cadmium is extremely toxic for the environment and it is imperious that it should be eliminated from waste waters. The classic methods of purification [5], [6] are not always efficient enough and the doing away with the traces in waters requires an economic solution.

The present work was directed towards selecting some bacterian strains capable of accumulating cadmium in order to employ them as microbiological collectors, for the removal of the traces of cadmium present in waste waters resulted from cadmium electroplating.

2. Experimental

Researches have been carried out on non-pathogenic bacteria isolated from the airmicroflora of a hospital section. Researches have been carried out on five strains belonging to the following species: *Bacillus cereus, Escherichia coli, Proteus vulgaris, Sarcina lutea* and *Pseudomonas aeruginosa.*

The cultures were kept on agar-agar media 0.5%, pH=7.2, incubated for 18 hr. at 37°C. The bacterian cultures obtained after transfering on the solid medium were harvested by washing with physiological saline solution (8.5‰) and were used for inoculating.

For the study of the accumulation capacity of the strains the inoculating was performed in Erlenmeyer flasks in 100 ml sample broth with pH= =7.2, Cd(II) in various concentrations and inoculation at 37°C. *Sarcina lutea* and *Escherichia coli* selected for a great accumulation capacity have been adapted to the cadmium contents of the medium, by their successive transfering for seven days on the solid medium that contains Cd(II) and have then been used in the study of the concentration capacity of Cd by their grown in the above mentioned conditions.

At the same time determinations have been made using a suspension of 5×10^7 microbian bodies/ml that has been introduced in a glucose—phosphate buffer in the presence of cadmium. These suspension have been obtained after inoculating on Roux plates (containing agar-agar media 2%, pH=7.2) and washing with a physiological saline solution.

For the researches we have used a standardised solution of Cd(II) that contains cadmium sulphate.

The results of the experiments were interpreted along the same lines as in previous papers [7].

3. Results and Discussions

3.1. Cadmium Accumulation by Direct Metabolization. Testing of Accumulation Capacity of Cadmium with Bacteria Isolated from Air Microflora

Bacillus cereus, Escherichia coli, Proteus vulgaris, Sarcina lutea and *Pseudomonas aeruginosa* have been grown in 100 ml simple broth, pH= =7.2 and 4.86 μg/ml Cd(II). After various intervals of time (1 ... 8 days) microbian bodies (mb) were separated from the medium and the contents of cadmium was analysed (Fig. 1).

In the interval 2 ... 6 days ~30% of cadmium present in the medium is accumulated by *Escherichia coli* (*a, b*) (curves *II, V*), *Sarcina lutea* (curve *IV*) and *Pseudomonas aeruginosa* (curve *VI*). As one can see in Fig. 1 after a period of time (3 ... 6 days), when the accumulation is constant, there occurs an increase in the percent of accumulated cadmium. This process might be due to a precipitation of Cd with the metabolism products released by bacteria in the medium. The strain of *Bacillus cereus* (curve *I*) showed a low accumulation capacity and the insignifiant the strain of *Proteus vulgaris* (curve *III*).

a) *The Influence of Cd(II) Concentration*

At the optimal accumulation time of Cd(II), *Escherichia coli* (*a*) and *Sarcina lutea* have been harvested after a previous growth in the presence of various concentrations of cadmium from 0.54 to 9.6 μg/ml in the culture medium. *Escherichia coli* (*a*) is at te most accumulated 37% at 4 μg/ml Cd(II) and *Sarcina lutea* 55% at 6.4 μg/ml (Fig. 2).

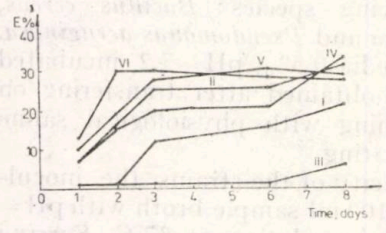

Fig. 1. — Cd(II) accumulation in time by various bacterium strains : *I — Bacillus cereus* ; *II—Escherichia coli* (*a*) ; *III — Proteus vulgaris* ; *IV — Sarcina lutea* ; *V—Escherichia coli* (*b*) ; *VI — Pseudomonas aeruginosa.*

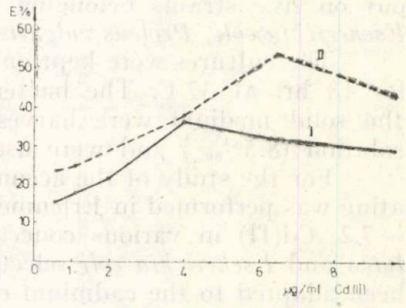

Fig. 2. — Infleuence of Cd (II) concentration : *I—Escherichia coli* (*a*) ; *II — Sarcina lutea.*

b) *Influence of the Amount of Inocul*

The dependence of Cd accumulation on the amount of various microbian bodies from 10^7 to 5×10^7 mb/ml different with *Escherichia coli* and *Sarcina lutea* (strains adapted and unadapted to Cd) might be explained as due to different metabolic and biochemical characteristics of the two strains belonging to various species (Fig. 3).

3.2. Cd(II) Accumulation by the Bacterian Mass Suspended in Glucose – Phosphate Medium

The bacterian suspension of 5×10^7 mb/ml was introduced in a phosphat buffer pH=6.3, glucose 2% and 1.3 μg/ml Cd(II) for five days. The accumulation rates obtained under these conditions are : *Sarcina lutea* 31%, *Escherichia coli* (*a*) 54% and *Escherichia coli* (*b*) 26%. The accumulation rates proves that *Escherichia coli* (*a*) is the fittest for Cd(II) concentration.

a) *Influence of pH*

The bacterian mass of *Escherichia coli* (*a*) that corresponds to $m=0.115$ g was suspended in 25 ml glucose–phosphate buffer with a pH=3.9 ... 9.1 and with 1.3 μg/ml Cd(II). A maximal accumulation of 44% is reached at pH=7.98 (Fig. 4).

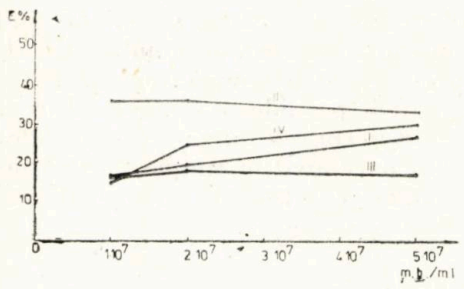

Fig. 3. – Influence of the amount of inocul on Cd(II) accumulation : *I* – *Escherichia coli* (*a*); *II* – *Sarcina lutea* (strains adapted to Cd(II)) ; *III* – *Escherichia coli* (*a*) ; *IV* – *Sarcina lutea* (strains unadapted to Cd (II)).

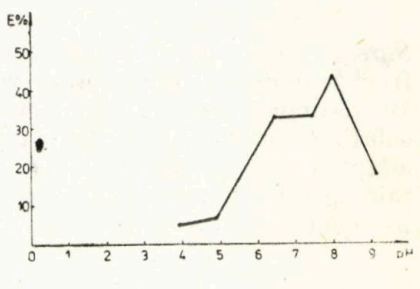

Fig. 4. – Influence of pH on Cd(II) accumulation with *Escherichia coli* (*a*).

b) *Time Influence*

Following up over six days Cd(II) accumulation with a suspension of *Escherichia coli* (*a*) ($m=0.1426$ g) one can find out that the accumulation is approximatively constant (within the limits of analysis errors) and has the value 50 ... 55%.

c) *Influence of* Cd(II) *Concentration*

Under optimal conditions of pH=7.98 for 48 hr. with an amount of bacterian mass that corresponds to $m=0.1426$ g, there is obtained, from diluted solutions 0.1 μg/ml Cd(II), an accumulation of 62% that decreased with the increase of concentration Cd(II) at 36% for 2.6 μg/ml Cd(II) (Fig. 5).

The complete removal of Cd from the solution can be achieved either by using a greater amount of bacterian mass or by resorting to a process

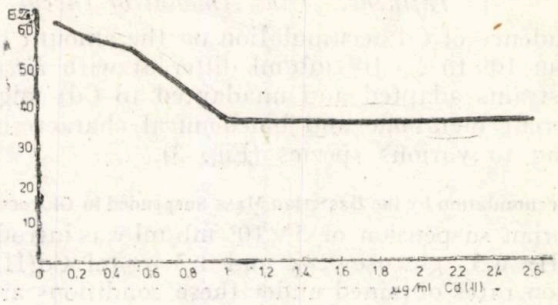

Fig. 5. — Influence of Cd(II) concentration on accumulation with *Escherichia coli* (*a*).

in multiple stages by introducing a new amount of bacterium mass in the solution left after centrifugation.

3.3. Removal of Cadmium from Waste Waters Resulting from Cadmium Electroplatig with Bacterian Strains

a) *Direct Metabolisation*

The results obtained proved that strains of *Escherichia coli* (*a*) and *Sarcina lutea*, experimented under certain conditions, can accumulate Cd(II) from a liquid medium (broth with a pH=7.2, at a temperature of 37°C). By resuming the process in several stages it is possible to remove Cd from solutions practically totally. Strains of *Escherichia coli* (*a*) and *Sarcina lutea* adapted and unadapted to Cd have been inoculated in simple broth containing Cd(II) 0.55 µg/ml from waste waters. The percent of Cd collected by bacteria is presented in Table 1.

Table 1

Removal of Cadmium from Waste Waters with Strains Adapted and Unadapted to Cadmium

Strains adapted	*E*, [%]	Strains unadapted	*E*, [%]
Sarcina lutea	74.1	*Sarcina lutea*	84.3
Escherichia coli (*a*)	84.3	*Escherichia coli* (*a*)	90.1
Escherichia coli (*b*)	14.5	*Escherichia coli* (*b*)	42.9

One can see that *Sarcina lutea* and *Escherichia coli* (*a*) can be employed as microbiological collectors for removing the Cd traces left in the solutions from processes of Cd electroplating after their having been purified by classic methods. The method is efficient and can be extended to the purification of waters containing traces of radioactive Cd. Bacteria adapted to Cd accumulate higher percentage that the unadapted ones. Adaptation to Cd may imply an alteration of the enzymatic equipment that favours the accumulation process of this element.

b) *Introduction of the Bacterian Mass in Glucose—Phosphate Buffer*

Having the optimal conditions previously determined (phosphate buffer pH=7.8, time 48 hr., glucose 2%) in the solutions containing Cd (II) from waste waters, there was introduced a bacterian mass corresponding to m=0.273 g. The results proved can be remove from 85% to 44% in solutions with a concentrations of Cd(II) from 0.24 to 0.96 μg/ml.

4. Conclusions

1. The capacity of accumulation of Cd(II) by some bacteria isolated from air microflora : *Bacillus cereus, Escherichia coli, Proteus vulgaris, Sarcina lutea* and *Pseudomonas aeruginosa* has been studied by growing the bacteria in the culture medium or by suspending the bacterian mass in a glucose—phosphate buffer in the presence of Cd(II).

2. By direct metabolization, after growing in simple broth (pH=7.2, 37°C, optimal time three days) *Escherichia coli* (*a*) accumulated Cd from solutions that contain 4 μg/ml at the most and *Sarcina lutea* 55% at 6.4 μg/ml.

3. Under the optimal conditions established experimentally (pH= =7.98, time 48 hr.) there is obtained by suspending the bacterian mass in glucose phosphate buffer 2% with an amount of mass of *Escherichia coli* (*a*) corresponding to m=0.1426 g an accumulation of 62%. The total removal of Cd(II) can be achieved either by initially using a greater amount of bacterian mass or by resorting to a process with multiple stages by introducing a new amount of bacterian mass in the solution left after centrifugation.

4. The obtained results show that *Sarcina lutea* and *Escherichia coli* can be employed as microbiological collectors for removing Cd(II) traces from solutions resulting from Cd electroplating after their purification by classic methods.

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ACUMULAREA Cd(II) CU COLECTORI MICROBIOLOGICI *ESCHERICHIA COLI* ŞI *SARCINA LUTEA*

(Rezumat)

S-a cercetat capacitatea de acumulare a Cd(II) de către unele bacterii izolate din aeromicroflora: *Bacillus ceraes, Escherichia coli, Proteus vulgaris, Sarcina lutea* şi *Pseudomonas aeruginosa*, prin dezvoltarea bacteriilor în mediul de cultură sau prin suspendarea masei bacteriene în tampon fosfat glucozat în prezenţa Cd(II). În acest scop s-au studiat condiţiile optime de pH, timp, concentraţia Cd(II) şi a masei bacteriene.

Rezultatele obţinute pun în evidenţă faptul că *Sarcina lutea* şi *Escherichia coli* pot fi întrebuinţate în calitate de colectori microbiologici pentru îndepărtarea urmelor de Cd(II) din soluţiile provenite de la cadmiere, după purificarea acestora prin metode clasice.

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BEITRÄGE ZUR ENERGETIK DER OBERFLÄCHEN ZEOLITISCHEN MOLLSIEBEN

VON

M. CRUCEANU und EVELINE POPOVICI

1. Vorwort

Die Synthesebedingungen haben ein wichtiges Einfluß über dem energetischen Zustand der Absorbtionsoberfläches der Mollsieben. Die Versuche über die Mollsieben, die durch hydrothermale Synthese mit Hilfe eines Ultraschallfedes synthetisiert wurden, zeigt die verschiedene Teilnahmegrade der anionische Teile bei die Bildung des Krystalline Gitter nach der Ausstrahlungszeit mit wichtige Einfluß über die Adsorbtionswermögen des Wassers.

Für Adsorbenten im allgemeinen und für die Mollsieben, in besonderen, ist das Adsorbtionsvermögen des Wassers eine für die Praxis sehr wichtige Eigenschaft und kann gleichzeitig bedeutende Informationen über sauensfähige Struktur und auch über die Oberfläche geben.

Wir meinen daß unter den Faktoren, die den energetische Zustand der Adsorbtionsoberfläche der Mollsieben beeinflussen, eine wichtige Rolle der Synthesebedingungen zufällt. Um diese Hypothese zu überprüfen, wurde Mollsieben durch hydrothermale Synthese präpariert und zwar während das Medium mit Hilfe eines Ultraschallfeldes intensiv agiert wurde.

2. Experimentelle Teile

Es wurden zwei Syntheseserien ausgeführt, in denen man wässerige Lösungen von Na-Silikat und -Aluminat mit der Bildung des Zeolithen entsprechende Zusamensetzung verwendete. In der ersten Serie war der Wert der dielektrische Konstante für alle Synthesen des Reaktionsmediums dergleiche [1]...[3] und es wurde nach der bekannten Technik vorgegangen. In der zweiten Serie wurde die Polarität des Mediums durch Hinzufügen von organischen Lösungsmittel verändert [4] ... [6]. In beiden Serien fanden die Synthese und die Kristallisation in einem Ultraschallfeld statt. Die erhaltenen Produkte wurden durch Filtrieren abgesondert und chemisch, strukturell und adsorbtiv untersucht [6].

3. Ergebnisse und Diskussion

Die Analyse der Produkte, die in der ersten Serie enstanden waren, hat zu den Angaben in Tabelle 1 geführt, wo man ein steigende Adsorbtionsvermögen des Wassers im Verhältnis zur Beschallungsdauer bemerkt.

Tabelle 1

Einige Merkmale der Produkte der ersten Serie

Produkt	Beschallungsdauer Min.	Chemische Zusammensetzung SiO_2/Al_2O_3	*Aa* %	*Ab* %	Bemerkungen
U1	10	2,30	24,8	2,56	*Aa*, *Ab* sind Werte für Adsorbtionswermögen des Wassers bzw. des Bensols.
U2	15	2,16	28,3	2,10	
U3	20	2,15	31,1	1,92	
U4	30	2,10	32,6	1,51	
U5	60	2,08	34,0	1,30	
U6	90	2,09	34,1	1,30	

Gleichfalls wird den Molekulargittercharakter durch das Sinken des Adsorbtionsvermögens des Bensol unterstrichen. Die difraktometrische Analyse zeigt, daß alle Produkte eine Struktur von Typ NaA haben. Gleichzeitig variabile Quantitäten von amorphen Phasen haben, welche aber nicht 10% überschrieten und dem Ansteigen der Beschallungsdauer kontinuerlich sinken.

Die Untersuchung der Produkte der zweiten Syntheseserie (konstante Chemischezusammensetzung und Beschallungsdauer, allerdings mit Hinzugaben der verschiedenen Lösungsmitteln) führten zu den Angaben der Tabelle 2.

Die difraktometrische Analyse zeigt, daß die Kristallinen Strukturen der Produkte sowol von denen der Bezugsprodukte (*U5*) als auch untereinender verschieden sind. Im Difraktogramm des Produktes *M3* erkent man das Zeolith Na—Zh, von J d a n o v [7] synthetisiert und veröfentlicht, und im Produkt *T3* erkennt man einen Fajazit [8]. Das Produkt *B3* enthält nur amorphe Phase, die allerdings in kleinen Mengen in jeden der anderen Produkte vorhanden ist. Die Interpretation der Ergebnisse im Bezug auf

Tabelle 2

Einige Merkmale der Produkte der zweiten Serie

Produkt	Beschallungsdauer Min.	Chemiche Zusammensetzung SiO_2/Al_2O_3	*Aa* %	*Bb* %	Lösungsmittel
U5	60	2,08	34,0	1,3	Wasser (W)
M3	60	2,18	22,0	4,6	W+Metanol
T3	60	2,37	19,1	9,8	W+Trietanolamine
D3	60	2,40	16,0	8,1	W+Dimetylformamid
E3	60	2,25	19,7	3,8	W+Monoetanolamine
B3	60	1,68	12,4	9,0	W+Tetrabutilamonium Hydroxid

das Adsorbtionsvermögen nur auf Grund der chemischen Zusammensetzung führt zu keinen bezeichnenden Korellationen (Tabelle 1, 2).

Wir sind der Meinung, daß die Wert des Adsorbtionsvermögens des synthetischen Zeolithen mit Mollsiebeneingeschaften nicht nur von der chemische Zusammensetzung, bzv. Verhältnis SiO_2/Al_2O_3 abgehängt, sonder vor allem von dem energetischen Zustand der Oberfläche, so wie sie sich während der Kristallisation ergibt. Barrer vermutet [9] in der Induktionsperiode der Kristallisationskeime die Existenz von Alumino-silizischen polygonalen Anionen, mit aus der Verbindungen Si—O und Al—O enstanden kannten, welche später, durch Raumeinrichtung, alle bekannten zeolithischen Strukturen bilden könne. Diese Hypothese angenommen, nehmen wir an, daß in Bedingungen unseres Experimentes, unter der starken Einwirkung der Kavitationskraft, zwischen den vorgeschlagenen Strukturen, nur die viereckige Möglichkeit Bestehens haben (Tabelle 3).

Tabelle 3

Viereckige Strukturelelements

Form	Zusammensetzung			Ladung	Symbol
	Al	Si	SiO_2/Al_2O_3		
	1	3	3,66	— 9	A-13
	2	2	1,21	— 10	A-22

Folglich konnte die kristalline Struktur der gebildeten Zeolithen nur aus den Anionen *A*-13 und *A*-22, die zu zwei Grentze in silizische Verhältnis von 3,66 bzw. 1,21 führen, herrühren. Da die erhaltenen Produkte Werte zwischen diesen Grenzwerten haben, führt eine einfache Rechnung zur Festlegung des Mitwirkungsgrades jedwelchen anionischer Art, zur Aufstellung des kristallinen Baues des erhaltenen Produkte. Im Bezug auf die Art *A*-22 geht aus der Tabelle 4 hervor, daß der Mitwirkungsgrad gleichzeitig mit der Beschallungsdauer gestiegen ist, während er bei gleichbleibenden Beschalungsdauer mit der Anwachsen der Polarität des hinzugefügen Lösungsmittel gefallen ist.

Tabelle 4

Der Mitwirkungsgrad der vierekige Anionen

Produkt / Anion	*U*1	*U*2	*U*3	*U*4	*U*5	*M*3	*T*3	*D*3	*E*3
A-22	55	61	61,6	63	65	60,5	52,5	51,5	57,5
A-13	45	39	38,4	37	35	39,5	47,5	48,5	42,5

Die Funktion des Abb. 1 leist eine Folge des gesteigerten mechanisches Gleichgewichtes, daß das Anion A-22 im Verhältnis zum Anion A-13 hat. In Wirklichkeit wird die Länge der Verbindungen Si—O und Al—O, welche 1,63 Å bzw. 1,72 Å betragen [10], dann sieht man daß A-22 ein gleichseitiges Viereck ist, während A-13 ungleichseitig ist. Deswegen zerstört sich während der Beschallung unter der Einwirkung der Kavitation das Anion A-13 progressiv, was zu einem prozentuellen Anwachsen des Anions A-22 führt.

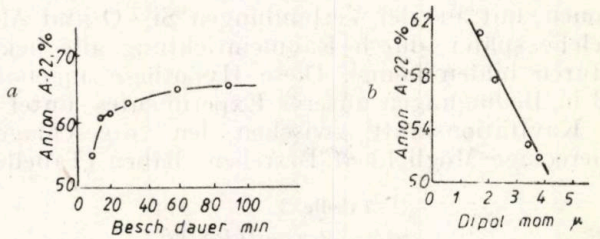

Abb. 1. — Der Mitwirkungsgrad des Anions A-22 bei der Bildung der Zeolithen in Ultraschallfeld : a — wässerige Medium im Bezug auf die Beschalungsdauer ; b — Wasser Lösungsmittel Medium im Bezug auf die dielektrische Konstante der Lösungsmittel.

Die Funktion des Abb. 1 b führt zur Annahme, daß im Reaktionsmedium gleichzeitig mit der mechanischen Zerstörung auch eine sonochemische Reaktion stattfindet :

$$2A\text{-}13 \rightleftarrows A\text{-}22 + 4\,\mathrm{Al}.$$

Das Gleichgewicht dieser Reaktion ist nach rechts verschoben wegen des Vorhandenseins der Lösungsmittel, die fähig sind, das aus der Reaktion enstandene Al-ion zu solvatieren.

Aus der gezeignete Mechanismus geht hervor, daß unter der Aktion des Ultraschalles bei der Bildung des kristallinen Aufbaues, die Mitwirkung des Anions A-22 der des Anions A-13 vorgezogen wurde. Weil sich diese beide Arten durch den Wert ihrer elektrischen Ladung unterscheiden (Tab. 3) ist zu erwarten, daß dieser Unterschied sich auch in den adsorbtiven Eingeschaften ihrer Oberflächen zeigt. Tatsächlich, wenn man die

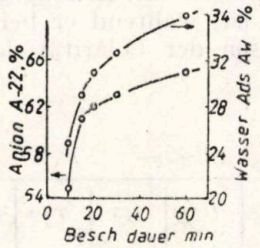

Abb. 2.—Die des Adsorbtionsvermögens und des Mitwirkungsgrades des Anions A-22 im Verhältnis zur Beschallungsdauer.

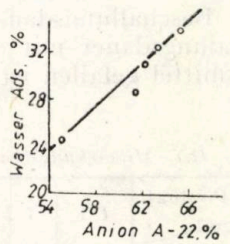

Abb. 3. — Veränderung des Adsorbtionsvermögens im Verhältnis zum Mitwirkungsgrad des Anions A-22.

Kurven des Abb. 2 vergleicht, kommt diese Tatsache zum Ausdruk, aber wenn Abb. 3 betrachtet, stellt man fest, daß zwischen dem Adsorbtionsvermögen des Wassers und dem Mitwirkungsgrad der Anionen Art *A*-22 eine positive Korrelation, linearer Art, von großer Intensität besteht.

Die gefundene Korrelation betrachten wir als ein Beweis zu unserer Hypothese, die Rolle der Ädificationsart der kristallinen Netzes über das Adsorbtionsvermögen der Molecularsieben betrifft. Gleichzeitig betrachten wir diese Korrelation als ein experimentelle Argument zur Hypothese R.M. Barrers hinsichtlich der hydrothermalen Synthese der Zeolithen.

4. Schlussfolgerungen

Ausser den sterischen und geometrischen Faktoren und der chemische Zusammensetzung usw., hängt das Adsorbtionsvermögen der Mollsieben auch von dem energetische Zustand der Oberfläche ab, während dieser von den Synthese Bedingungen abhängig ist.

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Lehrstuhl für generale Chemie
und Technologie

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CONTRIBUŢII LA ENERGETICA SUPRAFEŢEI SITELOR MOLECULARE ZEOLITICE

(Rezumat)

Printre factorii care influenţează starea energetică a suprafeţei de adsorbţie a sitelor moleculare, un rol important revine condiţiilor de sinteză. Cercetarea structural—adsorbtivă a sitelor moleculare preparate prin sinteză hidrotermală, în cîmp ultrasonor, a indicat un grad diferit de participare a speciilor anionice la alcătuirea edificiului cristalin, funcţie de durata de iradiere, cu influenţe majore asupra valorii capacităţii de adsorbţie a apei.

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CHIMIE ŞI INGINERIE CHIMICĂ

C.D. 661.832 ; 546.322.26 ; 661.312

RECHERCHES DE GÉNIE CHIMIQUE CONCERNANT L'OBTENTION DU SULFATE DE POTASSIUM PURIFIÉ, EN PARTANT DE L'HYDROXYDE DE POTASSIUM

I. L'ANALYSE DU PROCESSUS DE NEUTRALISATION

PAR

LIVIA IFRIM et AL. SZÉP

1. Introduction

Les produits de pureté avancée sont de plus en plus sollicités en différentes branches industrielles. L'obtention des ces produits est conditionnée, particulièrement, de la qualité des matières premières, mais également de la technologie de fabrication utilisée.

Pour la fabrication des tels produits à l'échelle industrielle actuellement on applique deux groupes de technologies [1], [2] ; schématiquement elles sont présentées dans les Fig. 1 et 2.

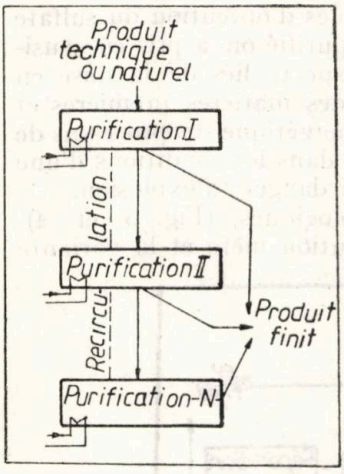

Fig. 1.—Le schéma technologique de purification par procédés physiques.

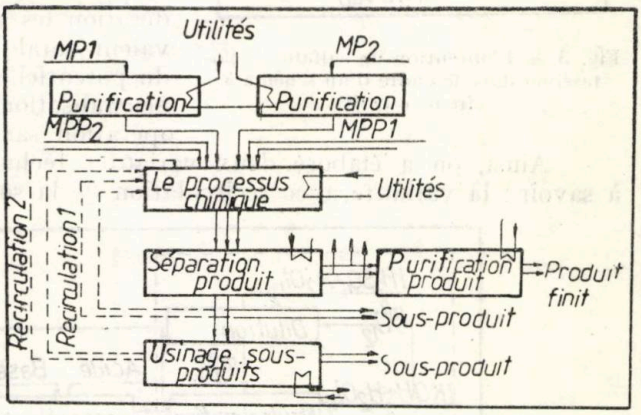

Fig. 2 — Le schéma technologique de purification par procédés chimiques.

Le choix de l'un des deux types de méthodes est déterminé par la réserve de matières premières, les caractéristiques de celles-ci, la qualité imposée au produit fabriqué et également le coût de la fabrication, en évidente dépendance avec l'importance social-économique du produit.

Le sulfate de potassium purifié este classifié dans le groupe des produits chimiques de qualité supérieure, qui doivent être réalises à l'échelle industrielle.

Les restrictions concernant la qualité du produit purifié se réfèrent non seulement au contenu en composant principal (98...99% K_2SO_4), mais particulièrement à la nature et au contenu des impuretés qui, dans quelques cas, sont très sévères (maximum 699 ppm Pb; maximum 100 ppm F ; maximum 3 ppm As ; maximum 1 ppm Cd, etc.). Par conséquent la technologie de fabrication doit assurer ces exigences.

De ce point de vue, dans ce qui suit on analyse le processus de la fabrication du sulfate de potassium purifié.

2. Matières premières. Schémas technologiques de fabrication

Pour la fabrication du sulfate de potassium sont nécessaires deux types de matières premières: l'un qui contienne du potassium et l'autre, de l'ion SO_4^{2-}.

En se basant sur l'analyse technico-économique et les exigences de qualité imposés au produit fini on a sélectionné, parmi les matières premières qui contiennent du potassium (KCl, KOH, K_2CO_3), l'hydroxyde de potassium solution et, de même, parmi celles qui contiennent de SO_4^{2-}, l'acide sulfurique technique obtenu à partir du soufre natif; ces substances peuvent assurer la pureté imposée au produit fini.

Pour établir les schémas technologiques possibles d'obtention du sulfate de potassium purifié on a pris en considération les aspects liés de la mise en valeur totale des matières premières et du potentiel énergétique du processus de neutralisation, dans les conditions d'une opération sans danger d'explosion.

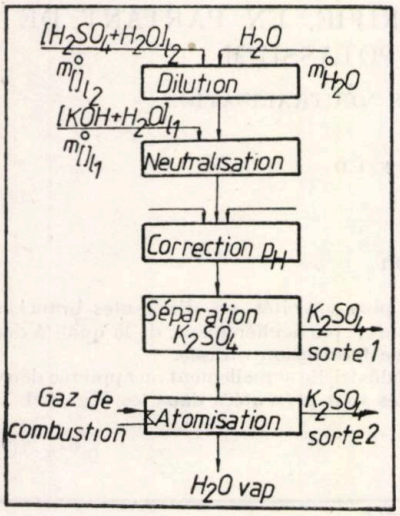

Fig. 3. — L'obtention du sulfate de potassium dans le cadre d'un schéma à circuit ouvert.

Ainsi, on a élaboré deux variantes technologiques, (Fig. 3 et 4), à savoir : la variante avec récirculation de la solution mère et la variante

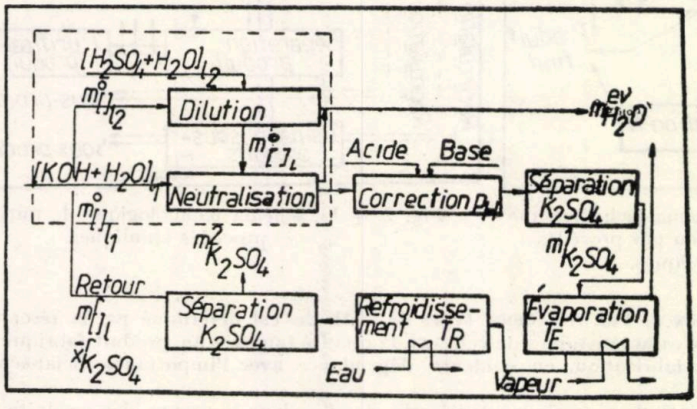

Fig. 4. — L'obtention du sulfate de potassium dans le cadre d'un schéma avec récirculation.

avec circuit ouvert. Pour les deux variantes technologique le processus se déroule en poursuivant les étapes principales ci-dessous : l'obtention de la solution diluée d'acide sulfurique, la neutralisation de la solution d'hydroxyde de potassium, la séparation du sulfate de potassium avec ou sans évaporation de l'eau. On précise le fait que, pour les deux variantes technologiques on obtient deux qualités différentes de sulfate de potassium.

3. L'analyse générale du processus

Pour fixer le schéma technologique le plus avantageux on a effectué plusieures recherches théoriques et expérimentales de laboratoire, pour établir les paramètres technologiques optima, la qualité du produit et également les consommations spécifiques, théoriques et réelles. En utilisant la méthode de l'analyse d'un processus technologique global [3], le processus a été divisé en processus technologiques composants et puis chacun a été décrit quantitativement par les modèles mathématiques de bilan de masse et thermique.

Les déterminations expérimentales réalisées à l'aide d'une installation de laboratoire ont permis l'obtention concrète des modèles mathématiques de bilan et la détermination des consommations spécifiques de matériaux et d'énergie.

Les aspects de génie chimique étudiés dans le cadre de cette analyse concernaient l'établissement des valeurs optima de la température de travail et de la concentration de la solution d'acide sulfurique (dans le cas du schéma avec récirculation et du rapport optimum de récirculation), dans les conditions de l'utilisation maximum de l'effet thermique en totale sûreté.

3.1. Le mécanisme macrocinétique du processus. Modèles mathématiques du bilan

Le processus de l'obtention du sulfate de potassium, dans le cadre du schéma avec récirculation, peut être représenté par l'intermède de l'équation caractéristique [3] :

$$(1)\qquad [KOH+H_2O]_{l_1}+[H_2SO_4+K_2SO_4+H_2O]_{l_2}\rightarrow[K_2SO_4]_s+[K_2SO_4+H_2SO_4+H_2O]_l+[H_2O]_g.$$

Les processus de transformation sont les suivants :

$$(2)\qquad 2KOH+H_2SO_4=K_2SO_4+2H_2O,$$

$$(3)\qquad K_2SO_{4[]_l}=K_2SO_{4[]_s},\qquad (4)\qquad H_2O_{[]_l}=H_2O_{[]_g}.$$

Du point de vue macrocinétique le processus appartient aux processus industriels du type : mélange moléculaire—réaction—formation et croissance de germes, ayant lieu une réaction intense exothermique (Fig. 5).

À partir des processus de transformation considérés on a élaboré les modèles mathématiques du bilan thermique, et du bilan de masse qui ont la forme donnée dans le Tableau 1. Par leur intermédiaire on a effectué l'analyse du processus de neutralisation.

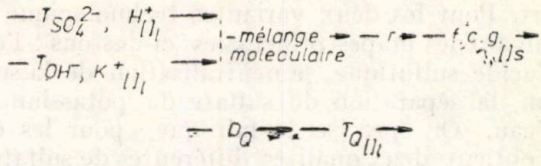

Fig. 5. — Le mécanisme macrocinétique du processus.

3.2. L'analyse du processus de neutralisation

Les données de l'équilibre liquide — solide dans le système H_2O—K_2SO_4 [4] indiquent une solubilité relativement diminuée du sulfate de potassium (10,03% K_2SO_4 à 20°C) et de petites augmentations de la solubilité à l'élévation de la température (24,1% K_2SO_4 à 100°C).

En même temps les déterminations de la valeur de l'effet thermique du processus montrent que la neutralisation des solutions de KOH avec les solutions concentrées d'acide sulfurique est accompagnée d'un dégagement notable de chaleur et comme conséquence, de l'évaporation d'une quantité d'eau et puis la séparation d'une certaine quantité de K_2SO_4 solide.

Afin de conduire en sûreté le processus (sans danger d'explosion) et pour l'utilisation au maximum du potentiel énergétique du celui-ci il est nécessaire de déterminer la valeure optimum des paramètres de travail, à savoir : la concentration de la solution de l'acide sulfurique, la température de travail (y compris le rapport optimum de récirculation de la solution mère dans le cadre du schéma avec récirculation), pour une certaine concentration de la solution de KOH.

On obtient la solution pour ce problème par la résolution simultanée des modèles mathématiques de bilan de masse et thermique et l'établissement de la valeur optimum des variables mentionnées ci-dessus en adoptant un certain critère d'optimisation.

En effectuant une telle analyse, dans les conditions du déroulement adiabatique du processus, par l'intermédiaire du calculateur, on a obtenu les résultats présentés dans le Tableau 2 et les Fig. 6 et 7.

À l'aide des données obtenues on peut aboutir aux conclusions suivantes :

a) L'effet thermique correspondant du processus de neutralisation augmente d'une façon linéaire avec l'élévation de la concentration de la solution d'acide sulfurique et peut assurer, dans les conditions du déroulement adiabatique du processus, l'évaporation de 25 ... 35% de l'eau présente dans la masse de réaction. Si à l'effet thermique de neutralisation on ajoute également l'effet de la dilution de l'acide sulfurique, la quantité de l'eau évaporée augmente avec approximativement 8 ... 10%.

b) Le degré de séparation du sulfate de potassium résulté dans le processus de neutralisation, $\eta^n_{K_2SO_4[]_l}$, est approximativement 80%, quand on utilise une solution d'acide sulfurique de 70% ; si on utilise une solution d'acide de 94 ... 96%, le degré de séparation atteint 85 ... 87% (les calculs sont effectués pour la température d'ébulition de la solution).

Tableau 1

Le modèle mathématique du bilan du processus

$$\bar{x}_{K_2SO_4[]_l}=0,1233+0,000715\,t_{[]l}\ ;\ m_{K_2SO_4[]_l}=m^0_{[]_{l_1}}\bar{x}^0_{KOH}\frac{M_{K_2SO_4}}{2\,M_{KOH}}\ ;$$

$$m_{H_2O[]_l}=m^0_{[]_{l_1}}(1-\bar{x}^0_{KOH})+m^0_{[]_{l_2}}(1-\bar{x}^0_{H_2SO_4})+m^0_{[]_{l_1}}\bar{x}^0_{KOH}\frac{M_{H_2O}}{M_{KOH}}\ ;$$

$$m_{K_2SO_4[]_l}=\frac{\dfrac{\bar{x}^0_{KOH}\dfrac{M_{K_2SO_4}}{2M_{KOH}}}{1+\dot{\bar{x}}^0_{[]_{l_2}}-\dot{\bar{x}}^{ev}_{H_2O}}-\bar{x}_{K_2SO_4[]_l}}{1-\bar{x}_{K_2SO_4[]_l}}(m^0_{[]_{l_1}}+m^0_{[]_{l_2}}-m^{ev}_{H_2O});$$

$$m_{[]_l}=\frac{1-\dfrac{\bar{x}^0_{KOH}\dfrac{M_{K_2SO_4}}{2M_{KOH}}}{1-\dot{\bar{x}}^0_{[]_{l_2}}-\dot{\bar{x}}^{ev}_{H_2O}}}{1-\bar{x}_{K_2SO_4[]_l}}(1+\dot{\bar{x}}^0_{[]_{l_2}}-\dot{\bar{x}}^{ev}_{H_2O})m^0_{[]_{l_1}}$$

$$\dot{\bar{x}}^0_{[]_{l_2}}=\frac{M_{H_2SO_4}}{2M_{KOH}}\cdot\frac{\bar{x}^0_{KOH}}{\bar{x}^0_{H_2SO_4}}\ ;\qquad m^{ev}_{H_2O}=(m^0_{[]_{l_1}}+m^0_{[]_{l_2}})\,\dot{\bar{x}}^{ev}_{H_2O}\ ;$$

$$c^0_{p_{[]_{l_1}}}T^0_{[]_{l_1}}+\dot{\bar{x}}^0_{[]_{l_2}}c^0_{p_{[]_{l_2}}}T^0_{[]_{l_2}}+H_{pr}=\dot{\bar{x}}^{ev}_{H_2O}h_{H_2O_{[]_g}}+\dot{m}_{[]_l}c_{p_{[]_l}}T_{[]_l}+\dot{m}_{[]_s}c_{p_{[]_s}}T_{[]_s}\ :$$

$$H_{pr}=\frac{\bar{x}^0_{KOH}}{2M_{KOH}}\Delta_R H^0_g-\dot{\bar{x}}^{ev}_{H_2O}\Delta H^{ev}_{H_2O}-m_{K_2SO_4[]_s}\frac{\Delta H_{crist}}{M_{K_2SO_4}};$$

$$\Delta_R H_g=\Delta_R H^0_{298}+\Delta H_{dissK_2SO_4}-\Delta H_{dissH_2SO_4}-2\Delta H_{dissKOH}\ ;$$

$$\Delta H_{dissK_2SO_4}=21,645+0,02177\,\dot{x}_{H_2O}\ ;\qquad \Delta H^{ev}_{H_2O}=3\,091,5-2,185\,T_{[]_l}\ ;$$

$$\Delta H_{dissKOH}=-23,75-8,0658\,\dot{x}^{01}_{H_2O}+0,63082(\dot{x}^{01}_{H_2O})^2\ ;$$

$$\dot{x}_{H_2O}=\frac{2M_{KOH}}{M_{H_2O}}\left(\frac{1+\dot{\bar{x}}^0_{[]_l}}{\bar{x}^0_{KOH}}-1\right);\qquad \dot{x}^{01}_{H_2O}=\frac{M_{KOH}}{M_{H_2O}}\cdot\frac{1-\bar{x}^0_{KOH}}{\bar{x}^0_{KOH}}\ ;$$

$$\eta^{G(n)}_{K_2SO_4}=\frac{1}{1+\bar{x}^{r(n)}_{K_2SO_4[]_l}/\dot{\bar{x}}_{[]_s}}\ ;\qquad \eta^{ev}_{H_2O}=\frac{m^{ev}_{H_2O}}{m_{H_2O_{[]_l}}}\ ;$$

$$\bar{x}^r_{K_2SO_4[]_l}=0,1233+0,000713\,T^r_{[]_l}\ ;\ \dot{\bar{x}}_{[]_s}=\frac{m_{K_2SO_{2[]_s}}}{m_{[]_l}}\cdot$$

Tableau 2

Les indicateurs du processus

Indicateur	Symbole	U/M	$\bar{x} = m_{[]_s}/m_{[]_l}$						
			0,25	0,50	0,75	1,00	1,50	1,85	4,0
Concentration de l'acide sulfurique après dilution	$\bar{x}^D_{H_2SO_4}$	kg/kg.sol.	0,1229	0,2179	0,2935	0,3550	0,4499	0,50	0,6925
Température théorique de l'acide après dilution	t	°C	40,42	58,45	73,50	84,47	105,48	116,44	140,12
La quantité de l'eau évaporée par voie autothermique	$m^A_{H_2O}$	kg / t.sol. KOH 45%	0	80	—	163	181	—	296
La quantité de K_2SO_4 séparée dans le processus de neutralisation	$m_{K_2SO_4}$	kg / t.sol. KOH 45%	0	156	—	309,47	364,0	397	500
Le degré théorique de séparation du K_2SO_4 dans le processus de neutralisation	$\eta^n_{K_2SO_4[]_l}$	%	0	20,43	—	44,61	54,36	64	80,4
La quantité de solution de recirculation	$m^r_{[]_l}$	kg / t.KOH 45%	2 485,6	1 242,8	828,5	621,4	414,2	335,9	155,35
Le degré de séparation globale du K_2SO_4 à 20°C	$\eta^G_{K_2SO_4[]_l}$	%	68,25	81,13	85,37	89,58	93,7	95,01	97,37

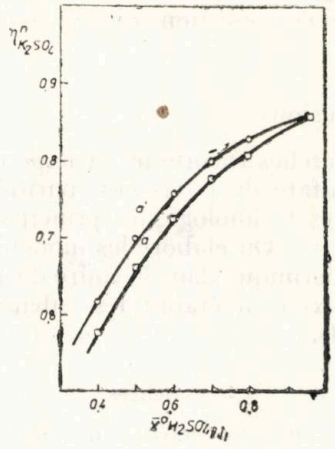

Fig. 6. — La variation du degré de séparation du sulfate de potassium : a — dilution isothermique de l'acide sulfurique; a' — dilution adiabatique de l'acide sulfurique.

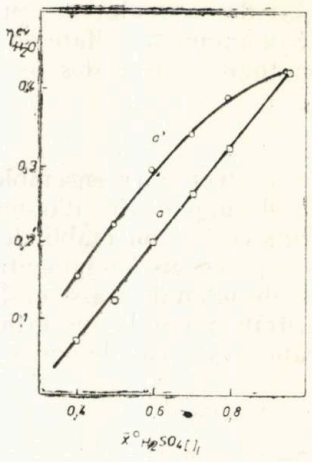

Fig. 7. — La variation du degré théorique d'évaporation de l'eau.

c) Les déterminations expérimentales effectuées à l'échelle de laboratoire montrent pourtant que l'utilisation de quelques solutions concentrées d'acide sulfurique, ($\bar{x}^0_{H_2SO_4}$=0,8 ... 0,94), n'assure pas la réalisation du processus de neutralisation dans les conditions de sûreté optima, par suite du danger d'explosion. Par conséquent on impose l'utilisation de certaines solutions d'acide sulfurique de 70 ... 75%. Dans ces conditions on peut réaliser un degré de séparation du sulfate de potassium de 80 ... 82% et une autoévaporation environ de 30% de l'eau présente dans la masse de réaction.

À partir de ces données on peut établir la valeur optimum du rapport de récirculation de la solution mère, dans le cadre du schéma à récirculation.

Les calculs du bilan effectués dans ce but montrent que pour réaliser un degré avancé de séparation du sulfate de potassium, avec des dépenses énergétiques minima, il est indiqué de travailler avec des débits de récirculation des plus petits. La diminution du débit de récirculation, cependant, attire l'élévation de la température de la solution d'acide sulfurique, obtenue après dilution, qui, dans le cas de certaines solutions ayant approximativement 80% acide sulfurique, atteint la valeur de la température d'ébullition (Tableau 2). La mise en contact de certaines solutions d'acide sulfurique se trouvant près ou à leur point d'ébullition avec la solution d'hydroxyde de potassium, présente de même le risque d'explosion. Pour cette raison on peut réaliser le processus en parfaite sûreté lorsque le débit de récirculation est plus grand et dans ce cas la chaleur dégagée est emmagasiné par la solution de retour. L'augmentation du débit de récirculation attire la diminution du degré de séparation du sulfate de potassium et en même temps, des dépenses de transport. Pour cette raison on impose le choix

d'un débit de récirculation optimum, qui peut déterminer l'obtention des quantités maxima de sulfate de potassium en conditions de dépenses minima et d'une totale sûreté des opérations.

4. Conclusions

On a effectué un ensemble de recherches théoriques et expérimentales de génie chimique, afin d'obtenir du sulfate de potassium purifié.

Dans ce but on établit les variantes technologiques principales et on analyse le processus fondamental de la ligne. On élabore les modèles mathématiques du bilan de masse et du bilan thermique dans le cadre du processus fondamental et par la résolution de ceux-ci on établit les valeurs optima des paramètres technologiques principals.

Notations

MP — matières premières ;
MP.P — matières premières purifiés ;
$\underline{x}_{Ai}$ — fraction molaire Ai ;
x_{Ai} — fraction massique Ai ;
$\underline{\underline{x}}$ — rapport molaire des composants ;
$\dot{x}$ — rapport massique des composants ;
η_{Ai} — degré de transformation ;
[ ] — symbole de la phase ;

Indices

0 — grandeur d'entrée ;
s, l, g — solide, liquide, gaz ;
D — dilution ;
r — récirculation ;
n — neutralisation.

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Chaire de Technologie chimique anorganique

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CERCETĂRI DE INGINERIE CHIMICĂ PRIVIND OBŢINEREA SULFATULUI DE POTASIU PURIFICAT, PLECÎND DE LA HIDROXID DE POTASIU

I. Analiza procesului de neutralizare

(Rezumat)

Se tratează, din punct de vedere teoretic şi experimental, procesul obţinerii sulfatului de potasiu de puritate ridicată, plecînd de la soluţii de hidroxid de potasiu şi acid sulfuric.

Se propun două variante tehnologice şi se analizează performanţele realizate în cadrul celor două scheme.

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D.C. 536.5 ; 66.063 ; 532

TEMPERATURE DISTRIBUTION IN FLOW OF THIN FILMS OF NON-NEWTONIAN FLUIDS OF HIGH VISCOSITY

BY

RADU Z. TUDOSE and FĂNICA MUSTAȚĂ

1. Introduction

Due to its advantages the flow in thin films is currently applied in up-to-date technologies using the evaporation, cooling, condensation, absorption, etc.

The heat transfer in flow of thin films of non-Newtonian liquids was less investigated [1], most of the reported papers concerning the Newtonian liquids [2]...[9].

In the present paper the theoretical and experimental distribution of the temperature in flow of non-Newtonian liquids of high viscosity on a flat vertical surface in the zone without waves is studied.

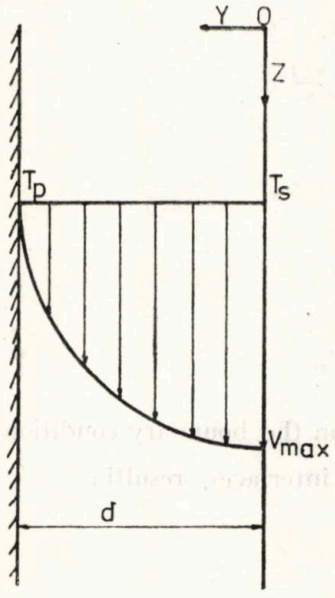

Fig. 1. — Physical model of the flow in thin films.

2. Theory

The physical model of the thin film flow in the smooth zone is depicted in Fig. 1. The origin of axis is taken at the film surface, the z-axis is oriented in the flow direction and the y-axis is normal to the surface.

The rheological equation describing the non-Newtonian behaviour has the form :

$$\tau_{yz} = -\eta^0 \left(\frac{dv_z}{dy}\right)^n. \tag{1}$$

For a non-Newtonian liquid, obeying the power law, in the zone of smooth flow, the equation of conservation of momentum, after simplification, can be writen as :

$$\frac{d\tau_{yz}}{dy} = \rho g. \tag{2}$$

By introducing the expression (1) into the Eq. (2) one obtains :

$$\frac{d}{dy}\left[-\eta^0\left(\frac{dv_z}{dy}\right)^n\right]=\rho g. \tag{3}$$

By integrating it results :

$$\left(\frac{dv_z}{dy}\right)^n=-\frac{\rho g}{\eta^0}y+C_1. \tag{4}$$

The integration constant is null for $y=0$, the Eq. (4) becoming :

$$\frac{dv_z}{dy}=-\left(\frac{\rho g}{\eta^0}\right)^{1/n}y^{1/n}. \tag{5}$$

For steady state the equation of energy, simplified for this type of flow, at a constant temperature of the heated surface, in expressed by :

$$-\lambda\frac{d^2T}{dy^2}=\eta\left(\frac{dv_z}{dy}\right)^2. \tag{6}$$

For a non-Newtonian liquid, obeying the power law, the relation

$$\eta=\eta^0\left(\frac{dv_z}{dy}\right)^{n-1} \tag{7}$$

is verified.

By introducing the relation (7) into the Eq. (6) one obtains:

$$\frac{d^2T}{dy^2}=-\frac{\eta^0}{\lambda}\left(\frac{dv_z}{dy}\right)^{n+1}. \tag{8}$$

Having in view the Eq. (5), Eq. (8) becomes :

$$\frac{d^2T}{dy^2}=\left(-\frac{\eta^0}{\lambda}\right)\left(-\frac{\rho g}{\eta^0}\right)^{\frac{n+1}{n}}y^{\frac{n+1}{n}}. \tag{9}$$

If we introduce the notation

$$k=\left(-\frac{\rho g}{\eta^0}\right)^{\frac{n+1}{n}}\left(-\frac{\eta^0}{\lambda}\right) \tag{10}$$

after the first integration the Eq. (9) leads to :

$$\frac{dT}{dy}=k\frac{n}{2n+1}y^{\frac{2n+1}{n}}+C_2. \tag{11}$$

The integration constant is determined from the boundary condition :

(12) for $y=0$, $dT/dy=0$ (flux zero at interface), resulting

$$C_2=0. \tag{13}$$

The Eq. (11) can be written as :

$$\frac{dT}{dy}=k\frac{n}{2n+1}y^{\frac{2n+1}{n}}. \tag{14}$$

After the second integration the Eq. (12) becomes :

$$T=k\frac{n}{2n+1}\cdot\frac{n}{3n+1}y^{\frac{3n+1}{n}}+C_3. \tag{15}$$

The integration constant, C_3, is determined with the following boundary condition :

$$\text{for } y=\delta,\ T=T_p. \tag{16}$$

It results :

$$C_3=T_p-k\frac{n}{2n+1}\cdot\frac{n}{3n+1}\delta^{\frac{3n+1}{n}}. \tag{17}$$

By substituting the constant C_3 into the Eq. (13) it results :

$$T-T_p=k\frac{n}{2n+1}\cdot\frac{n}{3n+1}\left(y^{\frac{3n+1}{n}}-\delta^{\frac{3n+1}{n}}\right) \tag{18}$$

For the boundary condition :

$$y=0,\qquad T=T_s \tag{19}$$

the Eq. (16) is converted into

$$T_s-T_p=-k\frac{n}{2n+1}\cdot\frac{n}{3n+1}\delta^{\frac{3n+1}{n}}. \tag{20}$$

By denoting the dimensionless temperature by :

$$\theta_{i,r}=\frac{T_p-T}{T_p-T_s}. \tag{21}$$

the ratio of the Eqs. (16) and (18) has the following form :

$$\theta_{i,r}=1-\left(\frac{y}{\delta}\right)^{\frac{3n+1}{n}}. \tag{22}$$

For Newtonian liquids ($n=1$) :

$$\theta_{i,r}=1-\left(\frac{y}{\delta}\right)^{4}. \tag{23}$$

3. Experimental

The experimental equipment, described in a previous paper, is constituted mainly of a heat exchange tube of $\varnothing=44\times3$ mm diameter and 2 000 mm length.

The non-Newtonian liquid flows as thin film on the external surface of the tube, heated with hot water flowing in the tube. The two fluids flow in counter-current.

On the surface of the heat exchange tube nine Cooper—Constantan thermocouples have been mounted. The temperature distribution in the

Table 1

Variation of the Solution Densities with Temperature for the Solutions of Polyethylene Oxide 4 000

T, [°C]	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
ρ, [kg/m³] $c=46\%$	1 091	1 090	1 089	1 087	1 085	1 084	1 083.5	1 083	1 082.5	1 082	1 081.5	1 081	1 081	1 080	1 079.5	1 079
ρ, [Kg/m³] $c=56\%$	1 070	1 069	1 068	1 067	1 065	1 064	1 063	1 062	1 061	1 060	1 059	1 058	1 057.5	1 057	1 057	1 056

Table 2

Variation of the Consistency (acording of the Ostwald de Waele Law) *with Temperature for Solution of Polyethylene Oxide 4 000*

T, [°C]	25	28	30	32	34	36	38	40	42	44	46	Flow index
K, [g/cm²s^n], $c=46\%$	0.110	0.106	0.106	0.096	0.094	0.090	0.085	0.072	0.067	0.063	0.060	0.98
K, [g/cm²s^n], $c=56\%$	0.236	0.204	0.201	0.168	0.155	0.194	0.122	0.108	0.105	0.1035	0.103	0.99

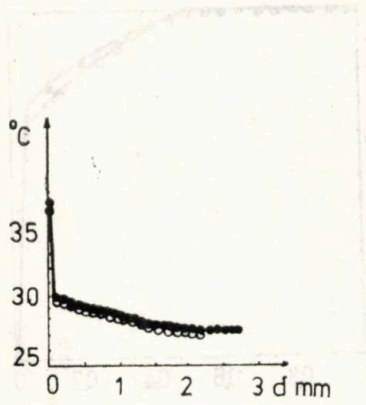

Fig. 2. — Variation of temperature vs. thickness at $\mathcal{R}e_{film}=580$, $\mathcal{R}e_{inlet}=18\,000$, $T_{film}=25°C$, $T_{inlet}=45°C$; length 30 mm (○), 130 mm (●) ; $c=56\%$.

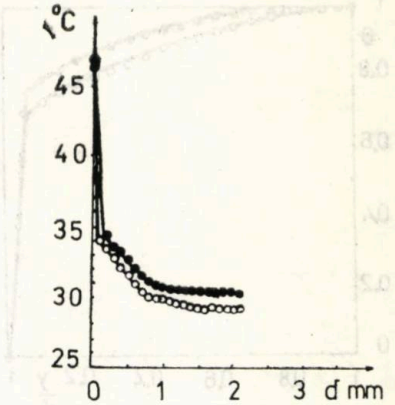

Fig. 3. — Variation of temperature vs. thickness at $\mathcal{R}e_{film}=490$, $\mathcal{R}e_{inlet}=18\,250$, $T_{film}=30°C$, $T_{inlet}=60°C$; length 30 mm (○), 130 mm (●); $c=56\%$.

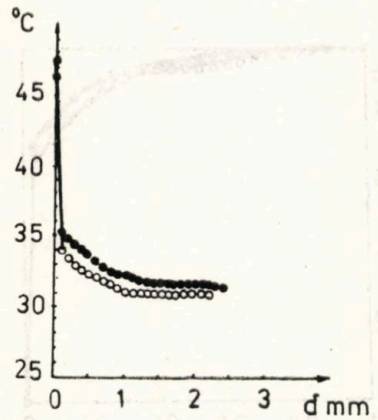

Fig. 4. — Variation of temperature vs. thickness at $\mathcal{R}e_{film}=650$, $\mathcal{R}e_{inlet}=18\,250$, $T_{film}=30°C$, $T_{inlet}=60°C$; length 30 mm (○), 130 mm (●) ; $c=56\%$.

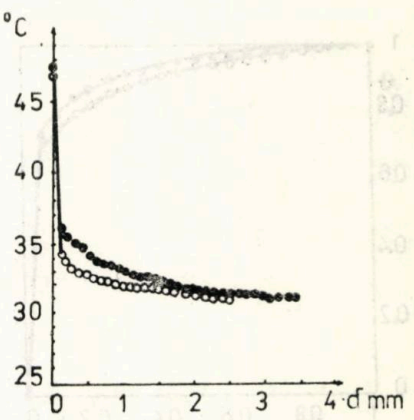

Fig. 5. — Variation of temperature vs. thickness, at $\mathcal{R}e_{film}=920$, $\mathcal{R}e_{inlet}=18\,250$, $T_{film}=30°C$, $T_{inlet}=60°C$; length 30 mm (○), 130 mm (●) ; $c=56\%$.

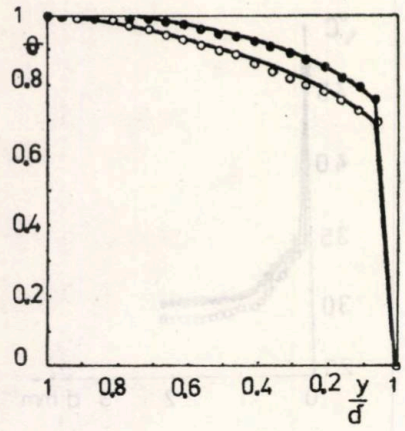

Fig. 6. — Variation of dimensionless temperature at $\mathcal{R}e_{film} = 580$, $\mathcal{R}e_{inlet} = 18\,000$, $T_{film} = 25°C$, $T_{inlet} = 45°C$; length 30 mm (○), 130 mm (●); $c = 56\%$.

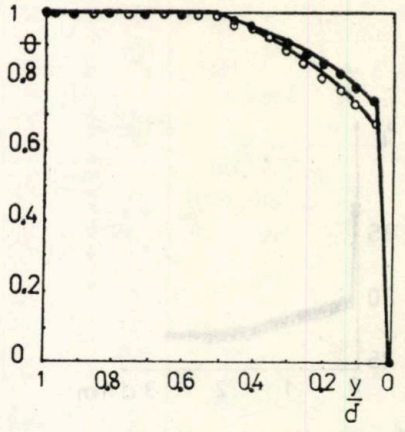

Fig. 7. — Variation of dimensionless temperature at $\mathcal{R}e_{film} = 490$, $\mathcal{R}e_{inlet} = 18\,250$, $T_{film} = 30°C$; $T_{inlet} = 60°C$; length 30 mm (○), 130 mm (●); $c = 56\%$.

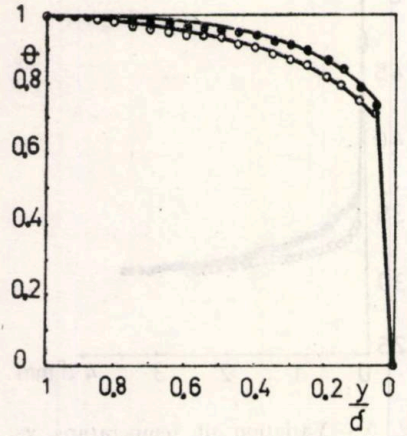

Fig. 8. — Variation of dimensionless temperature at $\mathcal{R}e_{film} = 650$, $\mathcal{R}e_{inlet} = 18\,250$, $T_{film} = 30°C$, $T_{inlet} = 60°C$; length 30 mm (○), 130 mm (●), $c = 56\%$.

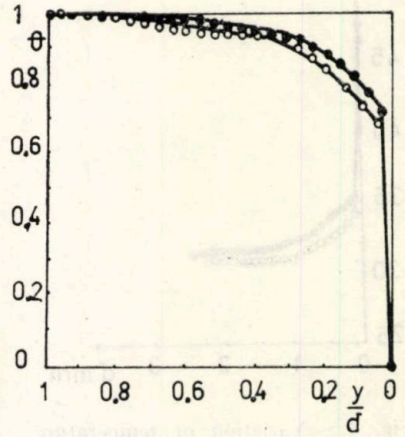

Fig. 9. — Variation of dimensionless temperature at $\mathcal{R}e_{film} = 920$, $\mathcal{R}e_{inlet} = 18\,000$, $T_{film} = 30°C$, $T_{inlet} = 60°C$, length 30 mm; (○), 130 mm (●); $c = 56\%$.

film was measured by a miniature thermocouple introduced into the liquid by means of a micrometric device. The temperature was measured at intervals of 10 μm. Two solutions of polyethylene oxide 4 000 (GIP, Brazi), with the characteristics listed in Tables 1 and 2, have been used as non-Newtonian liquids.

During the experiments the vertical position of the heat exchange tube has been kept constant. Any deviation from the vertical position can result in a nonuniform distribution of the liquid, followed by a nonuniform heating on the circumference.

The temperature profile for the two solutions has been measured at distances of 30 and 130 mm from the input zone, in the zone of smooth flow, for various Reynolds numbers of the film and of the heating fluid.

4. Results and Discussion

The experimental distribution of the temperature in the film at various Reynolds numbers is depicted in Figs. 2 ... 5 and the distribution of the dimensionless temperatures, under the same conditions, in Figs. 6 ... 9.

The Eqs. (22) and (23), expressing the dimensionless distribution of the temperature in the film, derived theoretically, are plotted in Fig. 10 for various n values (n is the flow index, according to the Ostwald de Waele law; $n=2$; 1,5 ; 1,0 ; 0,985 ; 0,96 ; 0,86).

It can be noticed that with decreasing flow index the Eqs. (22) and (23) approaches the optimum distribution in the experimental data. The largest variation of the temperature in the film is found to occur at a distance of about 10 μm from the metallic surface.

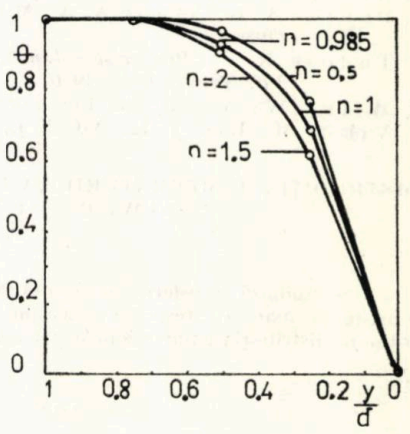

Fig. 10. — Graphical representation of the Eqs. (22) and (23).

5. Conclusions

The theoretical Eqs. of the temperature distribution in the film have a general character and depend on the flow indices, the distance from the interface and the film thickness.

The theoretical data obtained by means of Eqs. (22) and (23) are in good agreement with the experimental ones.

Notations

g — gravity acceleration, [m/s^2],
K — index of consistency, [N/m^2 . sec^n],
k — constant in equation (11),
n — flow index,
T — temperature, [°K],
T_w — wall temperature, [°K],

T_s — temperature of the film surface, [°K],
v_z — the flow-rate of fluid in the sense of flow, [m],
y — coordinate normal to the flow direction, [m],
z — coordinate in the flow direction, [m],
δ — film thickness, [mm],
η^0 — standard viscosity, [N/m^2 . sec^n],
η — viscosity, [N/m^2 . sec^n],
λ — thermal conductivity, [W/m.K],
$\theta_{i,r}$ — dimensionless temperature.

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DISTRIBUŢIA TEMPERATURII LA CURGEREA ÎN FILME SUBŢIRI DE LICHIDE NENEWTONIENE DE VÎSCOZITATE ÎNALTĂ

(Rezumat)

Se studiază transferul de căldură la curgerea în filme subţiri de lichide nenewtoniene de consistenţă mare ce respectă „legea puterii". Pornind de la un profil parabolic al vitezei este obţinută distribuţia adimensională a temperaturii în film.

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KINETICS OF DRYING OF ODORANT SUBSTANCES

BY

GH. CRISTIAN and I. TISU

1. Introduction

The studies carried out in the field of drying of materials evidenced the fact that the drying process is complicated by the diversity of physical characteristics of the materials and the presence of simultaneous heat and mass transfer.

The development mode of drying process is determined by moisture shifting inside the grain, by the energy required for its evaporation as well as by the moisture shifting through the material layer and the external boundary film.

The theoretical and experimental studies carried out in the field of material drying oriented towards settling the mechanism of the process. In the literature papers approaching the modelling of drying process are reported [1]...[5]. In the papers the process mechanism in the two periods is studied. Some investigators considered the moisture shifting to take place in vapour state while the others suppose as essential for these drying mechanism the moisture migration in liquid one. In the latter case, for the process of drying of materials bathed on the surface by the drying agent a general model and two particular ones have been derived [1].

In the present paper an experimental study on the drying of neroline by passing the drying agent over the material surface is reported. The curves of moisture distribution over the thickness of material layer during drying have been drawn and the influence of parameters of drying agent over the process kinetics has been studied.

The neroline is the methyl ether of β-naphthol and has a pleasant odor of orange flowers. It is used in perfumery compositions and in soaps. It is obtained by the etherification of β-naphthol with methanol in the presence of some specific catalysts (sulfuric acid, *p*-toluen sulphonic acid). From the reaction mass the product crystallisez by alcalinization with solution of natrium hydroxide. The crude neroline, separated by filtration and dried, is purified by steam distillation.

2. Experimental

2.1. Distribution of Moisture in the Material

The experimental studies have been carried out on a laboratory equipment formed of a tunnel dryer provided with a drying chamber and a chamber for air heating [1].

For determining the moisture distribution in the material layer, during the drying process, a gravimetrical procedure has been used [6],

[7]. For this purpose several cylinders of 23 mm diameter and 35 mm height have been confectionned. Each cylinder was formed of seven rings, with a 5 mm height (Fig. 1). The cylinders have been fixed in a parallelipipedic tray isolated on five faces with a thermoinsulating layer (raft layer). The tray was placed at the lower part of the drying chamber. For determining the moisture content the cylinders have been taken out at various time intervals and cut into seven parts. Each part was weighed on an analytical balance and introduced then into an oven for removing the remaining moisture.

The local moisture content has been determined by calculations and the curves of moisture distribution over the material thickness have been drawn. The obtained results are depicted in Fig. 2.

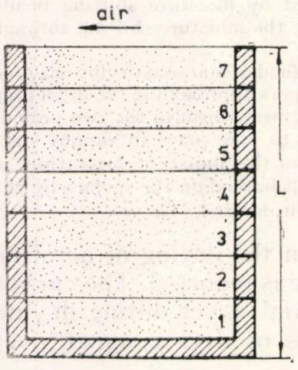

Fig. 1. — Cylinder for determining the moisture content.

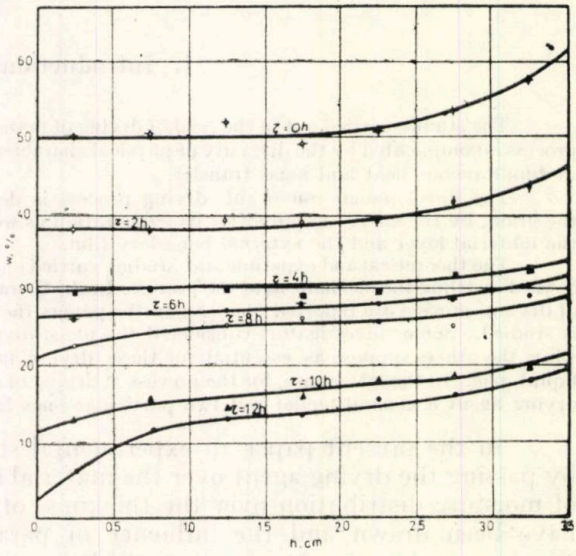

Fig. 2. — Curves of moisture distribution within the material.

The curves of moisture distribution have been determined at the temperature of drying agent of 60°C and a flow rate of 2.35 m/s.

The analysis of the curves plotted in Fig. 2 indicates the moisture migration to take place over the whole thickness of the material. The moisture migrates in liquid state from the lower layers of the material towards its surface, where the evaporation takes place. In this way a moisture gradient occurs over the material thickness which determines the moisture migration.

As long as the migration rate of moisture from inside the material towards the surface is higher than the rate of evaporation, the material surface will be continuously fed with the moisture from the internal layers. The resistance to the process will be located in the boundary layer at the material surface. After about 12 hours from the beginning of the drying

process the rate of moisture migration from inside the material becomes lower than the evaporation rate at the surface, which determines the moisture decrease at the material surface until the equilibrium moisture. From this moment the evaporation surface shifts into the material which results in the occurence of two zones in the material — an external dry zone and an internal humide zone.

The obtained experimental results indicated the neroline drying to take place according to the model with complete zone of moisture migration [1]. According to this model the drying proceeds in two stages : a stage of formation and another of disparition of the migration zone.

In the first stage the migration zone extends throughout the material thickness, the moisture at the surface decreasing until the equilibrium moisture. The attaining of the equilibrium moisture indicates the end of the first stage and the beginning of the second. In the second stage the moisture evaporation takes place at the surface between the two zones. The vapours formed diffuse through the dry zone and the external limiting film towards the mass of drying agent. The drying rate in the second stage decreases since to the resistance of external boundary layer the resistance to the vapour diffusion through the dry zone adds. The last resistance becomes the process determining step. The material drying can be considered finished off when at the lower part of the material layer the equilibrium moisture is reached.

2.2. Influence of the Parameters of Drying Agent on the Drying Kinetics

The drying of neroline was carried out by passing the drying agent over the material surface. For this purpose the neroline was placed in a plastics tray, insulated on five faces with raft layers and introduced then into the drying chamber. The variation with time of the removed water has been followed.

The parameters of drying agent influencing the process are : the temperature, the relative moisture and the flow rate. These parameters influence not only the drying rate but also the technological properties and the material quality.

Taking into account the influence of these parameters on the drying process, the drying regime has to be settled in such a way as to obtain the dry material with the required technological properties in a relatively short time and with minimum heat consumption.

From the parameters of drying agent which influence the process, in the present paper the temperature and the flow rate have been investigated. The hot air was used as drying agent.

To find the influence of air temperature on the kinetics of neroline drying, runs were carried out at three different temperatures namely, 40°, 50° and 60°C. The air flow rate was kept constant at 3.45 m/s. The obtained results are plotted as drying curves in Fig. 3.

As can be seen in Fig. 3, the drying of neroline takes place in two periods, one of constant drying rate, the other of continuously decreasing rate.

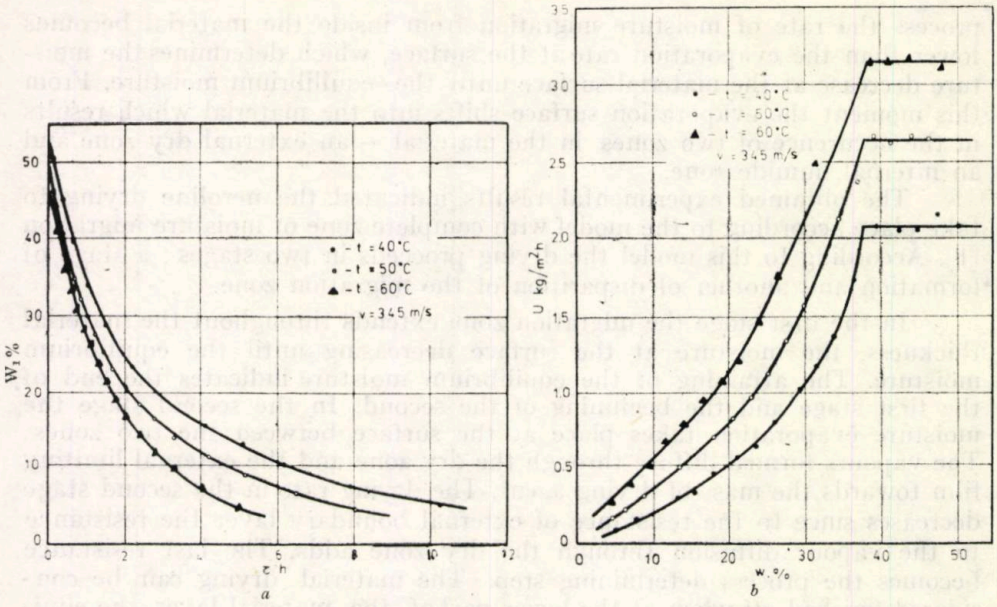

Fig. 3. — Kinetic curves of neroline drying : *a* — variation of material moisture with time ; *b* — variation of drying rate vs. moisture.

During the drying period of constant rate the rate of moisture evaporation at the material surface is comparable to those of evaporation at the free surface of the liquid. Due to the moisture gradient occuring over the material thickness, the material surface is fed with moisture from inside the material in all the period of constant drying rate.

During the period of decreasing rate the drying process is controlled by the rate of evaporation, the resistance to vapour diffusion through the dry layer of material and the external boundary layer. The resistance to vapour diffusion through the dry material layer significantly increases becoming the rate determining step.

In most cases the duration of the drying process is determined by the drying rate during the decreasing rate period.

The analysis of curves plotted in Fig. 3 indicate the drying rate to increase with increasing air temperature, which determines the shortening of the process duration. The influence of the air temperature is more pronounced during the period of constant drying rate than during the rate decreasing one.

To study the influence of air rate on the drying process runs were carried out at two different rates (1.72 and 3.45 m/s). The air temperature was kept constant at 60°C. The obtained results are plotted in Fig. 4.

As seen in Fig. 4 the rate of drying agent influences the rate of moisture removal from the material. The drying rate increases with increasing air rate. This influence is more pronounced in the period of constant drying rate than in the period of decreasing one. The weaker influence of the air rate in the period of constant drying rate can be accounted for by the fact

that the evaporation surface shifts inside the material which determines the occurence of an additional resistance to that of the boundary layer at the surface, corresponding to the period of constant drying rate. The air resistance influences the drying rate by means of the boundary

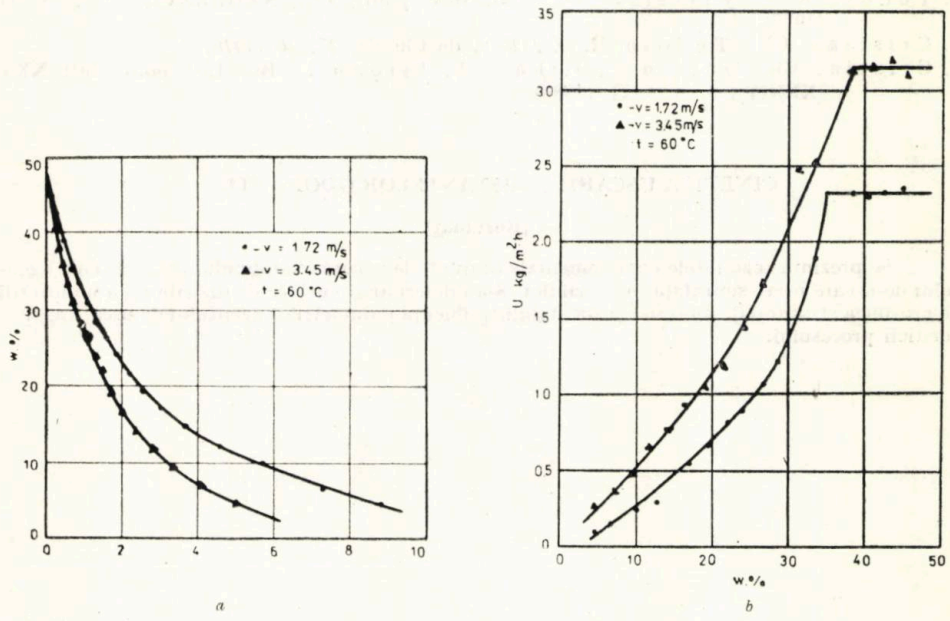

Fig. 4. — Influence of air rate on the drying kinetics : *a* — variation of the material moisture with time ; *b* — variation of drying rate vs moisture.

limit at the surface. It the latter resistance becomes to decrease, compared to the resistance of the dry material layer, which becomes predominant, the air rate is expected to have not the same influence as in the period of constant drying rate.

3. Conclusions

The experimental results of the studies concerning the neroline drying by the pass of the drying agent over the material surface allow the following conclusions to be drawn ;

1. The drying process has two periods; — a drying period of constant drying rate and another with continuously decreasing drying rate.

2. The increases in air temperature and rate determines the increasing of drying rate.

3. The curves of moisture distribution inside the material during the drying suggest the use of a model with complete zone of moisture migration.

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CINETICA USCĂRII SUBSTANŢELOR ODORANTE

(Rezumat)

Se prezintă rezultatele experiementale obţinute la uscarea nerolinului prin trecerea agentului de uscare peste suprafaţa materialului. S-au determinat curbele de distribuţie a umidităţii pe grosimea stratului de material şi s-a stabilit influenţa parametrilor agentului de uscare asupra cineticii procesului.

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DIE SUSPENSIONSPOLYMERISATION DES VINYLCHLORIDS MIT TEMPERATURPROGRAMM

SIMULATION DES THERMISCHEN VERHALTENS DES REAKTORS

VON

MATEI MACOVEANU und CORNELIU PETRILĂ

1. Die Polymerisation von Vinylchlorid in Suspension bei konstanter Reaktionsgeschwindigkeit

Die Suspensionspolymerisation von Vinylchlorid in industriellem Maßstab stellt noch eine Reiche schwieriger Probleme, infolge des nichtstationären Charakters hinsichtlich der zeitlichen Schwankung der Geschwindigkeit der Polymerisationsreaktion.

Das schwierigste Problem ist in solchen Fällen, beim Entwurf der Reaktoren und SCALE-UP die Bestimmung der Wärmeaustauschflächen, da die Polymerisationswärme meistens beachtenswert ist. Deshalb muß beim Entwurf der Wärmeaustauschflächen die größte aus der Reaktion hervorgehende Wärmemenge berücksichtigt werden.

Demnach werden in der Durchführung einer Charge weder der vorteilhafte Rauminhalt des Reaktors, noch die Wärmeaustauschfläche unter den besten Bedingungen angewandt. Der Reaktor wird übergroße Ausmaße haben und die wirtschaftliche Leistung geringer sein.

Es ist wünschenswert, daß solche, hinsichtlich der zeitlichen Schwankung der Polymerisationsgeschwindigkeit nichtstationär verlaufende Polyreaktionen mit konstanter Geschwindigkeit geführt werden, was den Entwurf des Reaktors bedeutend erleichtert und die beste Anwendung des Reaktionsraums für den gesamten Verlauf des Prozeßes sichert.

Zur Kontrolle der Reaktionsgeschwindigkeit bei der Suspensionspolymerisation des Vinylchlorids wurden einige, noch nicht genugend untersuchte Methoden vorgeschlagen, wie z.B. :

a) Anwendung von Initiatorengemischen mit verschiedenen Halbwertzeiten [1], [2].

b) Injecktion des Vinylchlorids (frisches Monomer) in den Reaktor in dem Augenblick, wo die Drucksenkung beobachtet wird [3].

c) Einführung von schwachen Inhibitoren ins Reaktionsmedium [4], [5].

In allen Fällen wird die Polymerisationstemperatur konstant gehalten.

Ausgehend von der Temperaturabhängigkeit der Konstanten der Reaktionsgeschwindigkeit, wurde eine neue Methode für die Kontrolle der Reaktionsgeschwindigkeit vorgeschlagen [6], [7], u.zw. die Anwendung eines Temperaturprogramms, das eine zeitliche lineare Variation der Polymerisationsgeschwindigkeit sichert. Mit andern Worten, eine lineare Schwankung der zeitlichen Konversion, wobei die Entstehung einiger, von der Reaktionszeit unabhängiger Wärmemengen erzielt wird.

Das Temperaturschwankungsprogramm wurde sowohl mittels einer empirischen Methode, von den Versuchskurven Konversion—Zeit [6] ausgehend, festgesetzt, als auch auf Grund eines kinetischen Modells [7]. Auf diese Weise entsteht die Möglichkeit, den Polymerisationsprozeß von Vinylchlorid in Suspension mit konstanter Reaktionsgeschwindigkeit auf dem Rechner zu führen.

Zwecks Beschreibung der in einem diskontinuierlichen Reaktor bei der Suspensionspolymerisation des Vinylchlorids stattfinden, den Grunderscheinungen wurde eines mathematische Modell ausgearbeitet [8]. Um das Gleichungssystem, welches das mathematische Modell des Polymerisationsreaktors bildet, auf dem Rechner zu lösen, wurde ein FORTRAN-Programm

[8] entworfen, welches die Einprägung der zeitlichen Werte der Konversion ermöglicht sowie auch der Polymerisationsgeschwindigkeit, der Reaktionstemperatur, der Temperatur des Abkühlmittels, der Reaktionswärme, der durch die mit Verkleidung versehenen Fläche des Reaktors ausgetauschten Wärme und der durch die verkleidungslose Fläche ausgetauschten Wärme, für die beiden Leitungsverfahren des Polymerisationsprozeßes : bei konstanter Temperatur und mit konstanter Polymerisationsgeschwindigkeit unter Anwendung eines entsprechenden Temperaturprogramms.

2. Die Simulationsbedingungen der Polymerisation

Mit Hilfe des für den diskontinuierlichen Polymerisationsreaktor aufgestellten mathematischen Modells wurden einige Arbeitsbedingungen simuliert, und zwar : Anwendung von Initiatoren mit verschiedenen Halbwertzeiten, sowie auch von verschiedenen Umdrehungsgeschwindigkeiten des Agitators.

Zuerst wurde als Initiator das Lauroilperoxyd angenommen, welches folgende Geschwindigkeitskonstante der Dissoziationsreaktion [9] aufweist :

$$k_d = 1{,}353 \cdot 10^{19} \exp(-15\,810/T), \tag{1}$$

wo T — Polymerisationstemperatur.

Dieser Initiator wurde weitgehend bei der Suspensionspolymerisation des Vinylchlorids angewendet und, obwohl er ein langsamer Initiator ist, wird er noch in einer Reihe von älteren Einrichtungen gebraucht.

Ein zweiter, in Betracht gezogene Initiator war Di(sek-butil)-peroxydikarbonat mit der Konstanten [9] :

$$k_d = 1{,}478 \cdot 10^{17} \exp(-13\,680/T). \tag{2}$$

Dieser Initiator gehört zur Klasse der Peroxydikarbonate die schnelle Initiatoren sind und bei den neueren Einrichtungen mit für hohe Polymerisationsgeschwindigkeiten, also kurzfristige Chargen, entworfenen Polymerisationsreaktoren angewendet werden.

Die Rotationsgeschwindigkeit des Agitators betrug 80, bzw. 120 U/Min. Alle anderen Bedingungen blieben konstant [8].

Für die beiden Leitungsverfahren der Polymerisationsreaktion, bei konstanter Temperatur und mit konstanter Geschwindigkeit, wurden die Daten hinsichtlich des Reaktorverhaltens vom Standpunkte des Wärmebetriebs aus unter den oben angeführten Bedingungen analysiert.

3. Darstellung and Verwertung der Daten

In Abb. 1 wird die Konversionsvariation für die vier in Betracht gezogenen Fälle dargestellt : schneller Initiator und konstante Temperatur von 55°C, langsamer oder schneller Initiator und konstante Geschwindigkeit von 33%/Stunde, schneller oder langsamer Initiator und konstante Geschwindigkeit von 15%/Stunde und langsamer Initiator und konstante Temperatur von 55°C.

Es ist interessant zu unterstreichen, daß die für den Verlauf der Polymerisation mit konstanter Geschwindigkeit bis zum Erreichen der Endkonversion notwendige Zeitspanne dieselbe ist, gleichgültig, ob ein lang-

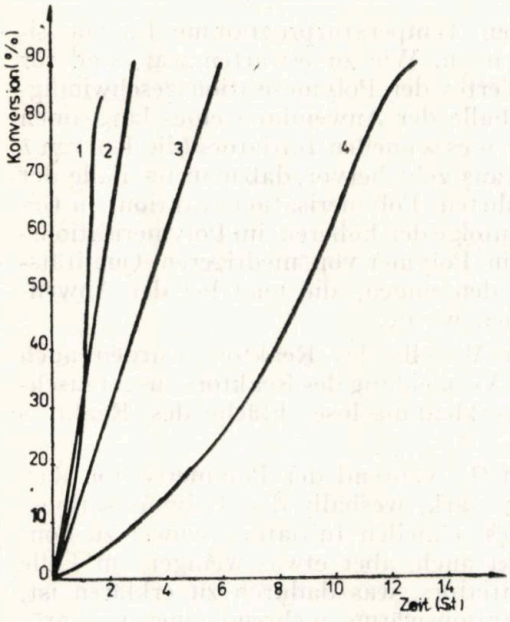


Abb. 1. — Zeitliche Schwankung der Konversion bei der Suspensionspolymerisation des Vinylchlorids : *1* — Di(sek-butil)peroxydikarbonat, T = = konst. = 55°C ; *2* — Lauroilperoxyd oder Di (sek-butil)-peroxydikarbonat und konstante Polymerisationsgeschwindigkeit (33% / Stunde) ; *3* — Lauroil oder Di (sek-butil) - peroxydikarbonat und konstante Polymerisationsgeschwindigkeit (15%/Stunde) ; *4* — Lauroilperoxyd, T=konst.= = 55°C ;

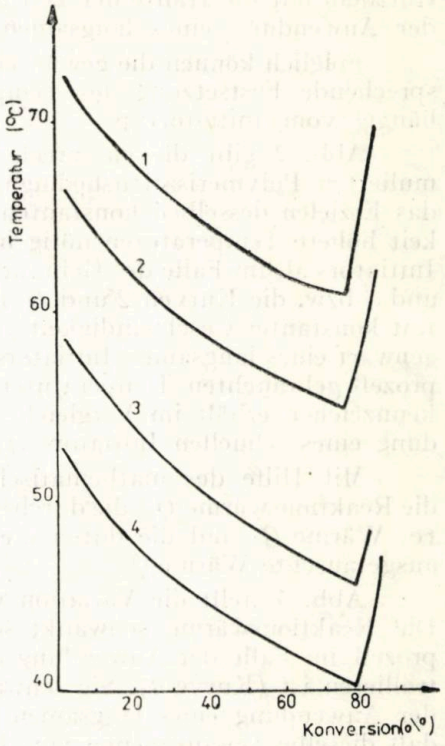


Abb. 2. — Die programmierte Variation der Polymerisationstemperatur im Falle des mit konstanter Reaktionsgeschwindigkeit geführten Prozeßes : *1*—Lauroilperoxyd ; Reaktionsgeschwindigkeit 33%/Stunde ; *2* — Lauroilperoxyd ; Reaktionsgeschwindigkeit 15%/Stunde ; *3* — Di(sek-butil)-peroxydikarbonat ; Reaktionsgeschwindigkeit 33%/Stunde ; *4* — Di(sek-butil)-peroxydikarbonat ; Reaktionsgeschwindigkeit 15%/Stunde.

samer oder ein Schneller Initiator angewendet wird (Abb. 1). Natürlich, wird für jeden Fall ein entsprechendes Temperaturprogramm festgesetzt welches das Beibehalten eines konstanten Wertes der Polymerisationsgeschwindigkeit sichert.

Aus Abb. 1 ist ersichtlich, daß bei einer Führung mit konstanter Geschwindigkeit von 33% Stunde, unabhängig vom gebrauchten Initiatortyp, die für das Erreichen einer Konversion von 95% notwendige Polymerisationszeit vergleichbar ist mit derjenigen, die im Falle der Polymerisation bei konstanter Temperatur, in Gegenwart des schnellen Initiators angegeben wurde.

Die Führung der Polymerisationsreaktion mit einer konstanten Geschwindigkeit von 15%/Stunde, obwohl sie längere Zeit beansprucht, füllt

trotzdem nur die Hälfte der Zeit aus, die für eine Charge nötig ist im Falle der Anwendung eines langsamen Initiators.

Folglich können die gewünschten Polymerisationszeiten durch die entsprechende Festsetzung des Temperaturprogramms erzielt werden, unabhängig vom Initiatortyp.

Abb. 2 gibt die entsprechenden Temperaturprogramme für die simulierten Polymerisationsbedingungen an. Wie zu erwarten war, sind für das Erzielen desselben konstanten Wertes der Polymerisationsgeschwindigkeit höhere Temperaturen nötig im Falle der Anwendung eines langsamen Initiators als im Falle des Gebrauchs eines schnellen Initiators (die Kurven *1* und *3* bzw. die Kurven *2* und *4*). Daraus geht hervor, daß man im Falle der mit konstanter Geschwindigkeit geführten Polymerisationsreaktion, in Gegenwart eines langsamen Initiators, infolge der höheren, im Polymerisationsprozeß gebrauchten Temperaturen, ein Polymer von niedrigeren Qualitätskennzeichen erhält im Vergleich zu denjenigen, die man bei der Anwendung eines schnellen Initiators erzielen würde.

Mit Hilfe des mathematischen Modells des Reaktors wurden auch die Reaktionswärme Q_R, die durch die Verkleidung des Reaktors ausgetauschte Wärme Q_2 und die durch die verkleidungslose Fläche des Reaktors ausgetauschte Wärme Q_3.

Abb. 3 stellt die Variation von Q_R während der Polymerisation dar. Die Reaktionswärme schwankt sehr stark, weshalb der Polymerisationsprozeß im Falle der Anwendung eines schnellen Initiators schwer zu kontrollieren ist (Kurve *1*). Sie schwankt auch, aber etwas weniger, im Falle der Anwendung eines langsamen Initiators, was dadurch zu erklären ist, daß dieselbe Gesamtmenge von Reaktionswärme während einer viel größeren Zeitspanne erzeugt wird. Wie aus Abb. 3 hervorgeht, beobachtet man bei einer Konversion von 70% den „Wärmegipfel", welcher im Falle der industriellen Reaktoren sehr schwer zu verfolgen ist.

Werden schnelle Initiatoren angewendet ist ein besonderer Entwurf des betreffenden Reaktors angebracht, um die Kontrolle der Reaktion zu ermöglichen. Jedenfalls wird der Reaktor übergroße Ausmasse haben, eben aus dem Grunde, die Periode des „Warmegipfels" überschreiten zu können. Vor und nach dieser Periode ist die notwendige Wärmeaustauschfläche viel kleiner. Im Falle der Anwendung eines langsamen Initiators ist die Lage etwas besser, da die zeitliche Schwankung von Q_R geringer ist. Leider dauert es zu lange, bis die Endkonversion erreicht wird, was eine niedere Leistung des Reaktors bewirkt.

Die Kurven *2* und *3* (Abb. 3) beweisen, daß alle oben angeführten Schwierigkeiten durch die Anwendung eines entsprechenden, das Erzielen einer zeitlich konstanten Geschwindigkeit bestimmende Temperaturprogramms behoben werden, unabhängig davon, ob der Initiator ein langsamer oder ein schneller ist.

Abb. 4 stellt die Variation der Wärmemenge Q_2. Im Falle der Polymerisation bei konstanter Temperatur ist die Schwankung von Q_2 mit der Konversion sehr groß, wenn ein schneller Initiator gebraucht wird (die Kurve *5*) und viel geringer, wird ein langsamer Initiator angewendet (die Kurve *6*). Wird die Polymerisationsgeschwindigkeit passend gewählt (z.B.

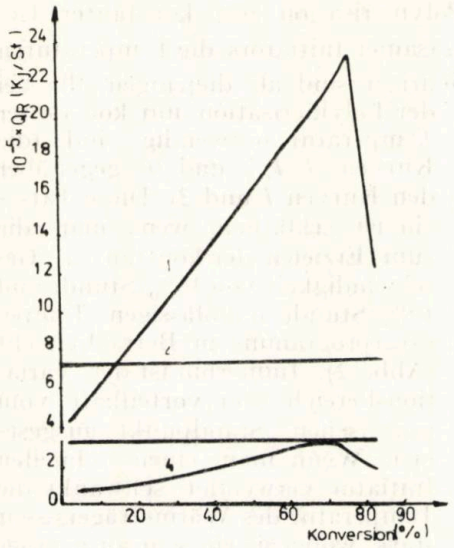


Abb. 3. — Die Variation der Reaktionswärme Q_R während des Polymerisationsprozeßes : *1* — Di(sek-butil)-peroxydikarbonat ; T = konst. = = 55°C ; *2* — Di(sek-butil)-peroxydikarbonat oder Lauroilperoxyd ; Reaktionsgeschwindigkeit 33 %/ Stunde ; *3* — Di(sek-butil)-peroxydikarbonat oder Lauroilperoxyd ; Reaktionsgeschwindigkeit 15%/Stunde ; *4*—Lauroilperoxyd ; T = konst. = 55°C.

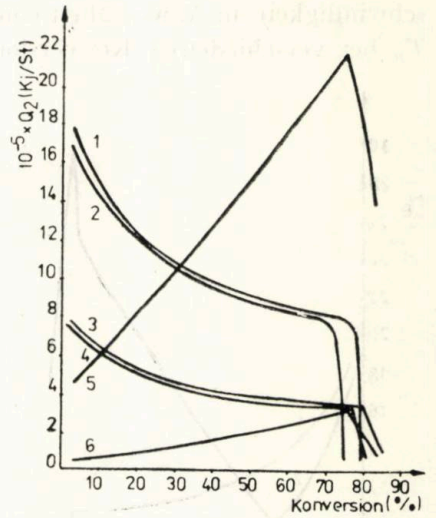


Abb. 4. — Die Variation der durch die mit Verkleidung versehene Reaktorfläche ausgetauschten Wärmemenge Q_2 : *1* — Di(sek-butil)-peroxydikarbonat ; Reaktionsgeschwindigkeit 33%/Stunde ; *2* — Lauroilperoxyd ; Reaktionsgeschwindigkeit 33%/ Stunde ; *3* — Di(sek-butil)-peroxydikarbonat ; Reaktionsgeschwindigkeit 15%/ Stunde ; *4* — Lauroilperoxyd; Reaktionsgeschwindigkeit 15%/Stunde ; *5* — Di(sek-butil)-peroxydikarbonat ; Reaktionsgeschwindigkeit bei 55°C ; *6*—Lauroilperoxyd ; T = konst. = 55°C.

15%/Stunde für die Kurven *3* und *4*), bemerkt man, daß die Variation von Q_2 langsam und gering ist bis zur Grenzkonversion, wo sie plötzlich fällt. Die Feststellung ist gültig unabhängig vom Initiatortyp.

Aus Abb. 5 ist leicht ersichtlich, daß im Falle der Anwendung eines langsamen Initiators (die Kurven *1* und *2*) und bei einem mit konstanter Geschwindigkeit geführten Prozeß die durch die verkleidungslose Reaktorfläche ausgetauschte Wärmemenge Q_3 größer ist als im Falle der Polymerisation in Anwesenheit eines schnellen Initiators. Demnach ist es wichtig, die Wirksamkeit des Wärmeaustausches durch die verkleidungslose Reaktorfläche zu erhöhen, für den Fall der Polymerisation mit konstanter Geschwindigkeit in Anwesenheit eines langsamen Initiators.

Es wird festgestellt, daß gleichzeitig mit dem Absinken der konstanten Reaktionsgeschwindigkeit von 33%/Stunde auf 15%/Stunde auch die ausgetauschte Wärmemenge Q_3 geringer wird, unabhängig vom verwendenten Initiatortyp (die Kurven *1*, *2* und *4*, *5*).

Was die Temperaturschwankung des Wärmeträgers aus der Reaktorverkleidung betrifft (T_R), in Abhängigkeit von der Konversion, ist aus

Abb. 6 erkennbar, daß im Falle der Polymerisation mit konstanter Geschwindigkeit, in Anwesenheit eines langasamer Initiators, die Temperaturen T_R bei verschiedenen Konversionen niedriger sind als diejenigen, die bei der Polymerisation mit konstanter Temperatur notwendig sind (die Kurven *3*, *4*, *7* und *10* gegenüber den Kurven *1* und *2*). Diese Tatsache ist erklärlich, wenn man die zum Erzielen der konstanten Geschwindigkeit von 33%/Stunde und 15%/Stunde unablässigen Temperaturprogramme in Betracht zieht (Abb. 2). Immerhin ist der Variationsbereich sehr vorteilhaft vom praktischen Standpunkt ausgesehen. Wenn man einen schnellen Initiator verwendet, schwankt die Temperatur des Wärmeträgers sehr stark, wobei sie ein sehr ausgeprägtes Minimum im Falle der Polymerisation bei konstanter Temperatur aufweist (die Kurven *5* und *6*), was dazu führt, daß eine große Wärmemenge in sehr kurzer Zeit abgegeben werden muß, während die Variation von T_R der mit konstanter Geschwindigkeit geführten Polymerisation viel geringer ist (die Kurven *8*, *9*, *11* und *12*) und in einen viel leichter auszuübenden Bereich eingeht; die Werte sind kleiner als diejenigen, die bei der Polymerisation mit konstanter Geschwindigkeit in Anwesenheit eines langsamen Initiators nötig sind. Wird eine vorteilhafte Polymerisationsgeschwindigkeit gewählt (z.B. 15%/Stunde, die Kurven *8* und *9*), ist die Variation von T_R sehr gering bis zu hohen Konversionen und geht in einen sehr günstigen Temperaturbereich ein. Von diesem Gesichtspunkt aus müßen die Vorteile der mit konstanter Geschwindigkeit, in Anwesenheit eines schnellen Initiators geführten Polymerisation unterstrichen werden. In allen Fällen erleichtert eine größere Umrührgeschwindigkeit (U_R=120 U/Min. gegenüber 80 U/Min.) den Wärmeaustausch und erfordern weniger niedrige Temperaturen des Wärmeträgers aus der Verkleidung (die Kurven *1*, *3*, *5*, *7*, *8* und *11* gegenüber den Kurven *2*, *4*, *6*, *9*, *10* und *12*).

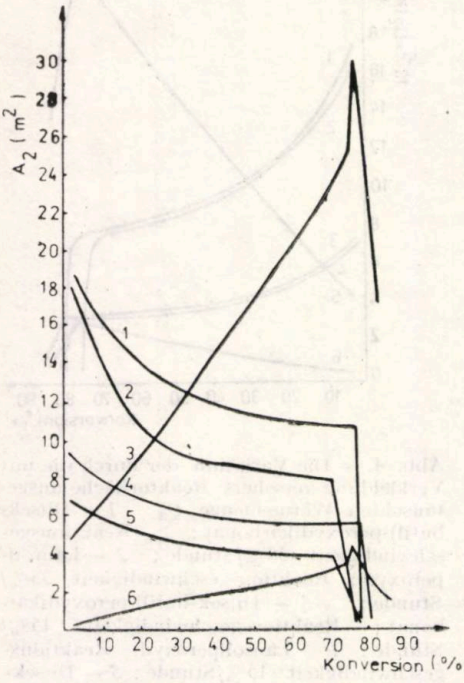


Abb. 7. — Die Variation der für den Wärmeaustausch durch die Reaktorverkleidung notwendigen Fläche (A_2), wenn T_R = konst. = 5°C: *1* — Di(sec-butil) - peroxydikarbonat; Reaktionsgeschwindigkeit 33%/Stunde; *2* — Lauroilperoxyd; Reaktionsgeschwindigkeit 33%/Stunde; *3* — Di(sec-butil) - peroxydikarbonat; T = konst. = 55°C; *4* — Di (sec-butil)peroxydikarbonat; Reaktionsgeschwindigkeit 15%/Stunde; *5* — Lauroilperoxyd; Reaktionsgeschwindigkeit 15%/Stunde; *6* — Lauroilperoxyd; T = konst. = 55°C.

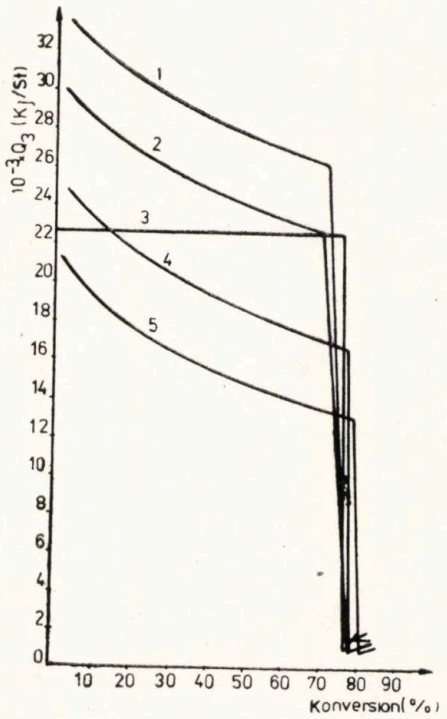


Abb. 5. — Die Variation der durch die verkleidungslose Reaktorfläche ausgetauschte Wärmemenge Q_3: *1*—Lauroilperoxyd ; Reaktionsgeschwindigkeit 33 %/Stunde ; *2* — Lauroilperoxyd ; Reaktionsgeschwindigkeit 15%/Stunde ; *3* — Lauroilperoxyd oder Di (sec-butil)-peroxydikarbonat ; T = konst. = 55°C ; *4* — Di(sec-butil)-peroxydikarbonat ; Reaktionsgeschwindigkeit 33%/Stunde ; *5*— Di(sec-butil)-peroxydikarbonat ; Reaktionsgeschwindigkeit 15%/ /Stunde.

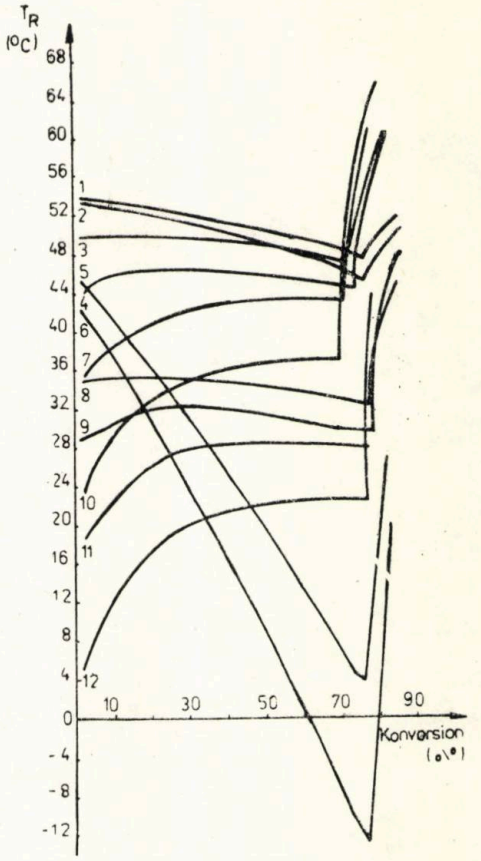
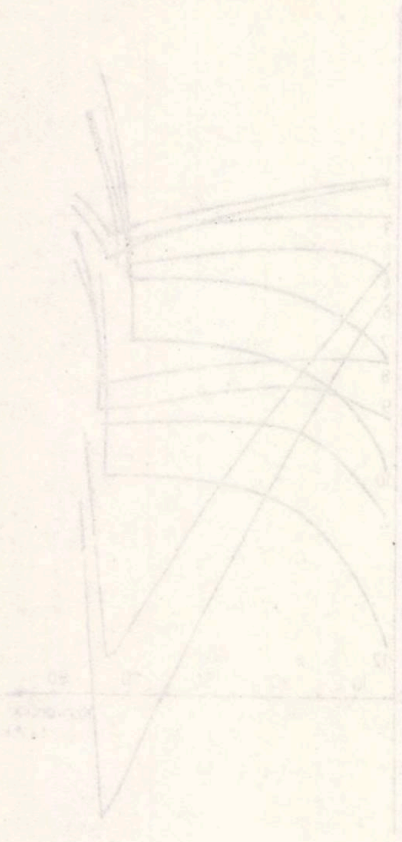


Abb. 6. — Die Variation der Temperatur des Wärmeträgers (T_R) aus der Reaktorverkleidung in Abhängigkeit von der Konversion : *1* — Lauroilperoxyd ; T = konst. = 55°C ; U_R = 120 U/Min ; *2* — Lauroilperoxyd ; T = konst. = 55°C ; U_R = 80 U/Min ; *3* — Lauroilperoxyd ; Reaktionsgeschwindigkeit 15%/Stunde ; U_R = = 120 V/Min ; *4* — Lauroilperoxyd ; Reaktionsgeschwindigkeit 15 %/Stunde ; U_R = 80 U/Min ; *5* — Di(sec-butil)-peroxydikarbonat ; T = konst. = 55°C ; U_R = 120 U/Min; *6* — Di (sec-butil)-peroxydikarbonat; T=konst.=55°C; U_R = 80 U/Min ; *7* — Lauroilperoxyd ; Reaktionsgeschwindigkeit 33%/Stunde ; U_R = 120 U/Min ; *8* — Di(sec-butil) - peroxydikarbonat ; Reaktionsgeschwindigkeit 15%/Stunde ; U_R = =120 U/Min; *9*—Di(sec-butil)-peroxydikarbonat; Reaktionsgeschwindigkeit 15%/Stunde ; U_R = =80 U/Min; *10* — Lauroilperoxyd ; Reaktionsgeschwindigkeit 33%/Stunde; U_R = 80 U/Min ; *11* — Di (sec-butil)-peroxydikarbonat ; Reaktionsgeschwindigkeit 33%/Stunde ; U_R = 120 U/Min ; *12* — Di(sec-butil)-peroxydikarbonat ; Reaktionsgeschwindigkeit 33%/Stunde ; U_R = = 80 U/Min.



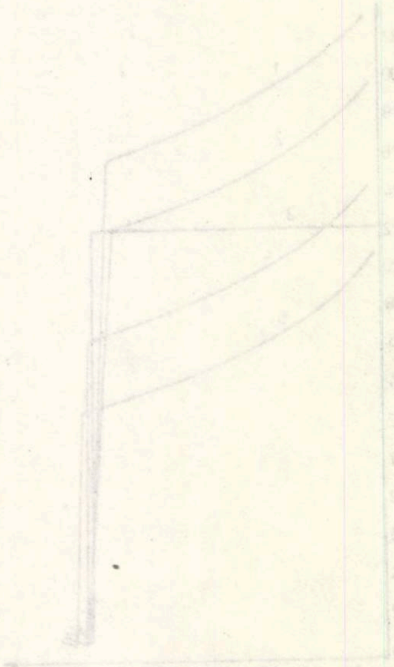


Abb. 7 zeigt die Variation der für den Wärmeaustausch durch die Reaktorverkleidung notwendigen Fläche (A_2), angenommen, daß die Temperatur des Wärmeträgers konstant und gleich 5°C ist.

Wird ein schneller Initiator gebraucht, so ist die notwendige Größtfläche A_2 viel kleiner bei der mit konstanter Geschwindigkeit geführten Polymerisation als bei der Polymerisation mit konstanter Temperatur (die Kurven *1*, *4* gegenüber der Kurve *3*). Die Variation von A_2 ist ebenfalls viel kleiner, vor allem für die Polymerisation mit konstanter Geschwindigkeit von 15%/Stunde (die Kurve *4*).

Wird ein langsamer Initiator angewendet, hat A_2 einen größeren Wert, wenn die Polymerisation mit Temperaturprogramm geführt wird im Vergleich zur Polymerisation mit konstanter Temperatur (die Kurven *2* und *5* im Vergleich zur Kurve *6*).

Durch die Führung der Polymerisation mit konstanter Geschwindigkeit von 15%/Stunde (die Kurve *5*) wird eine geringere Variation von A_2 gesichert im Vergleich zur Führung des Prozeßes bei konstanter Temperatur (die Kurve *6*), sowie auch ein wirksamerer Gebrauch der Wärmeaustauschfläche während des Verlaufs des Prozeßes.

4. Schlussfolgerungen

a) Bei der Führung der Suspensionspolymerisation des Vinylchlorids mit konstanter Geschwindigkeit ist die Reaktionsdauer dieselbe, unabhängig vom angewendeten Initiatortyp.

Das für die Erhaltung des festgelegten konstanten Wertes der Polymerisationsgeschwindigkeit notwendige Temperaturprogramm wird jedoch vom angewendeten Initiator bestimmt.

b) Der Gebrauch eines langsamen Initiators bietet einfachere Bedingungen zur Entfernung der Reaktionswärme, verlangt aber eine längere Reaktionsdauer im Falle der Polymerisation bei konstanter Temperatur und für die mit konstanter Geschwindigkeit geführte Polymerisation ein Temperaturschwankungsprogramm, das sich in einem Bereich mit zu hohen Werten befindet, als daß die Erziehung eines Polymers mit hohen Qualitätscharakteristiken möglich sie.

c) Die Anwendung eines schnellen Initiators stellt Probleme hinsichtlich der bei konstanter Temperatur geführten Polymerisation infolge der großen, in einer sehr kurzen Zeitspanne zu entfernenden Wärmemenge.

Die Führung der Polymerisation mit konstanter Geschwindigkeit ermöglicht die Entstehung von zeitlich konstanten Wärmemenge während der Reaktion, was eine vollkommene Ausbeute des Reaktionsraums während der Gesamtdauer einer Charge sichert.

d) Bei einer stärkeren Umrührung entstehen bessere Bedingungen für den Wärmeaustausch, sowohl bei der mit konstanter Temperatur geführten Polymerisation als auch bei der Polymerisation mit konstanter Geschwindigkeit. Die Umrührgeschwindigkeit muß jedoch den beabsichtigten Eigenschaften des synthetischen Polymers angepaßt werden.

e) Wird ein entsprechender konstanter Wert der Polymerisationsgeschwindigkeit gewählt, unabhängig vom Initiatortyp, dann kann der

Prozeß leicht kontrolliert werden, sogar in vom Standpunkt ihrer Wärmeaustauschfähigkeit weniger gelungenen Reaktoren wobei günstige Reaktionszeiten und gute Qualitätskennzeichen des Polymers erzielt werden.

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Technische Hochschule, Jassy,
Lehrstuhl für chemisches Ingenieurwesen

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POLIMERIZAREA ÎN SUSPENSIE A CLORURII DE VINIL CU PROGRAM DE TEMPERATURĂ

Simularea comportării termice a reactorului

(Rezumat)

A fost simulată polimerizarea în suspensie a clorurii de vinil cu ajutorul unui model matematic al reactorului de polimerizare în suspensie a clorurii de vinil, pentru anumite condiții de reacție și anume: utilizarea unui inițiator de polimerizare lent sau rapid, precum și diferite viteze de rotație a agitatorului. În toate aceste cazuri s-a luat în discuție conducerea reacției de polimerizare la temperatură constantă și respectiv cu folosirea unui program de temperatură care să asigure o viteză de polimerizare constantă în timp.

Pentru cele două tehnici de conducere a polimerizării au fost analizate și interpretate datele referitoare la comportarea reactorului din punct de vedere termic în condițiile de reacție menționate.

Avantajele oferite de conducerea reacției de polimerizare cu viteză constantă, ca urmare a utilizării unui program adecvat de temperatură, sînt evidente.

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1,2,4-TRIAZOLIUM-YLURES

IX. RÉACTION DE CYCLOADDITION 3 + 2 DIPOLAIRE DES TRIAZOLIUM-PHÉNACYLURES SUR LES ESTERS CINNAMIQUES[1])

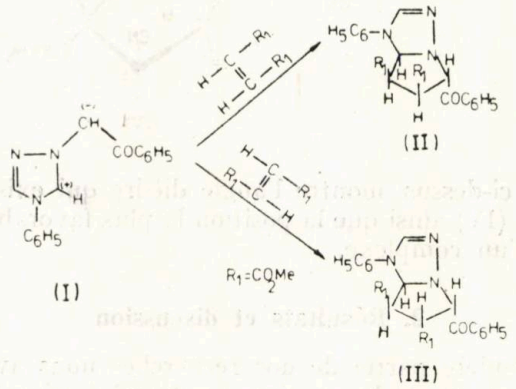
PAR

MAGDA PETROVANU, CRISTINA LUCHIAN et VIRGIL BĂRBOIU

1. Introduction

Dans des travaux antérieurs nous avons étudié la stéréochimie et la régiochimie des réactions de cycloaddition des phényl-4 triazolium-1, 2, 4 phénacylures avec les esters fumariques et maléiques [2], respectivement sur les oléfines *Z*-substituées [3] et les alcynes [4], [5].

Dans le cas de la réaction de l'ylure (I) avec le maléate et fumarate de méthyle on a démontré qu'on obtient deux produits stéréoisomères (II) et (III) [2] :



Dans la Fig. 1 on a représenté d'une part la disposition spatiale des protons des cycles pyrrolidiniques des produits (II) et (III), déterminés à l'aide de la RMN ^1H et on a donné, d'autre part, les déplacements chimiques δ, [ppm], et les constantes de couplage, [Hz].

Dans le cas de la réaction de l'ylure (I) avec l'acrylonitrile les données théoriques (perturbation de 2ème ordre) et spectrales RMN ^1H (utilisation de la technique des déplacements chimiques induits par le $Pr(fod)_3$) ont conduit à la conclusion que la réaction a lieu dans le sens contraire à celui

[1]) Note VIII v. [1].

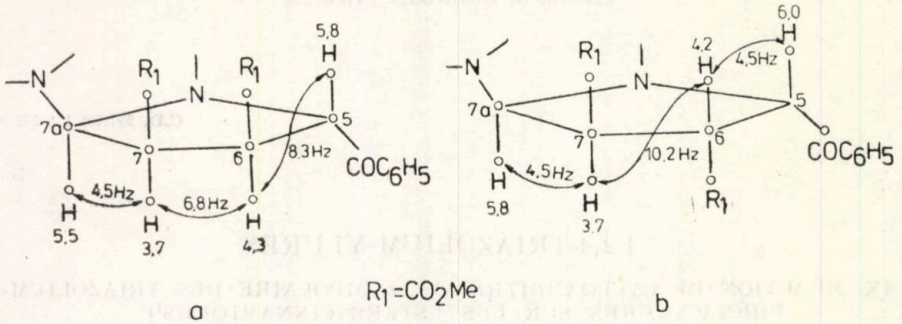
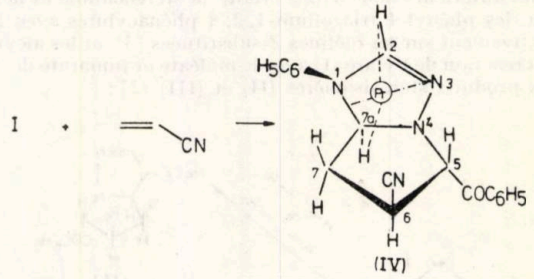


Fig. 1. — Distributions spatiales des protons appartenant aux cycles pyrrolidiniques : *a* — produit (II) ; *b* — produit (III).

dicté par la polarisation généralement acceptée dans les dipôles et les dipolarophiles [3]. Des situations analogues sont signalées dans la littérature [6].



Le schéma ci-dessus montre l'angle dièdre qui existe entre les deux cycles du produit (IV) ainsi que la position la plus favorable du praséodyme à la formation d'un complexe.

2. Résultats et discussion

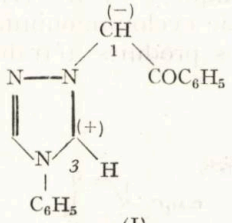
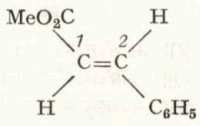
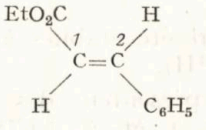
Dans le première partie de nos recherches nous avons effectué une étude théorique concernant la réaction du phényl-4 triazolium-1,2,4 phénacylure (I) avec les *trans* cinnamates d'éthyle et de méthyle en utilisant la théorie des perturbations du second ordre limitée aux orbitales frontières des réactifs [7], [8].

Les calculs des orbitales moléculaires ont été effectués par la méthode CNDO/2 [9]. La géometrie de l'ylure (I) nécessaire aux calculs a été déja présentée dans un mémoire précédent [3] et celles des cinnamates d'éthyle et de méthyle ont été approximées en utilisant les distances et les angles interatomiques standard.

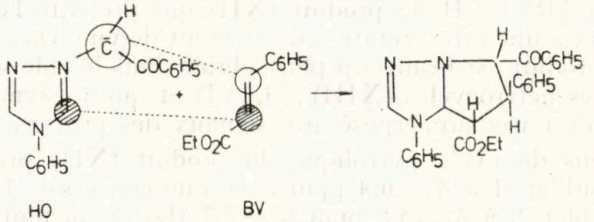
Le Tableau 1 indique les énergies des orbitales frontières et les coefficients des orbitales atomiques des atomes centres de réaction dans les orbitales frontières et les charges atomiques totales, Q.

Tableau 1

Résultats des calculs CNDO/2 concernant l'ylure (I) et les esters cinnamiques

Molécule	Orbitale et charge atomique totale	Énergie eV	Coefficients des orbitales atomiques, p_z	
			C_1	C_3
 (I)	H O	− 8,2811	+0,7019	−0,3583
	B V	2,2201	0,1008	0,4411
	Q		−0,2929	0,0576
			C_1	C_2
	H O	− 11,7272	0,4695	0,3306
	B V	1,0953	−0,4232	0,4738
	Q		−0,1121	0,0726
			C_1	C_2
	H O	− 11,6629	0,4673	0,3329
	B V	1,1445	−0,4248	0,4717
	Q		−0,1118	0,0713

Il ressort de l'examen de ce tableau que la réaction de l'ylure (I) avec le cinnamate d'éthyle (ou de méthyle) est HOMO controlée par rapport à l'ylure ($BV_{oléfine} - HO_{Ylure} = 9{,}42$ eV). Par conséquent, l'analyse des signes et des valeurs des coefficients des orbitales atomiques des atomes centres de réaction des orbitales HO-ylure et BV-ester cinnamique indique l'orientation représentée dans la Fig. 2 des réactants au cours de la réaction. Ici l'atome de carbone C_2, substitué par le phényle, du dipolarophile

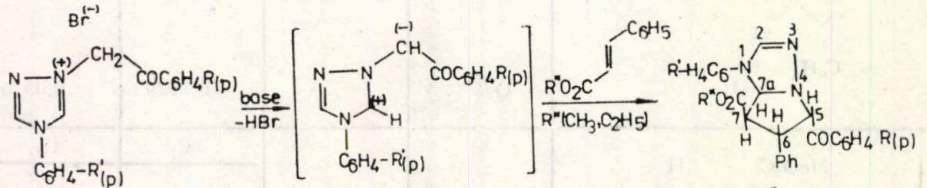


HO BV

Fig. 2. — Représentation orbitale de la réaction entre le triazolium-phénacylure (I) et le cinnamate d'éthyle.

se lie à l'atome de carbone ylurique. On peut donc aboutir à la conclusion que, selon les résultats du calcul, la cycloaddition analysée conduit à un seul adduit cyclique.

Dans le but de vérifier par voie expérimentale le déroulement de la réaction, établi théoriquement ci-dessus, nous avons étudiéles réactions des triazolium-phénacylure (I) avec les cinnamates d'éthyle et de méthyle et les réactions des triazolium-phénacylures (V) ... (VII) avec le cinnamate d'éthyle. Les réactions ont été effectuées en milieu chloroformique, les ylures (I), (V), (VI) et (VII) étant générés *in situ* à partir des sels de cycloimmonium correspondants et de la triéthylamine. On a obtenu les produits tétrahydropyrrolo-triazoliques (XII) ... (XVI) :



VIII (R=R'=H)
IX (R=NO_2; R'=H)
X (R=NO_2; R'=CH_3)
XI (R=OCH_3; R'=CH_3)

I (R=R'=H)
V (R=NO_2; R'=H)
VI (R=NO_2; R'=CH_3)
VII (R=OCH_3; R'=CH_3)

XII (R=R'=H; R"=CH_3)
XIII (R=R'=H; R"=C_2H_5)
XIV (R=NO_2; R'=H; R"=C_2H_5)
XV (R=NO_2; R'=CH_3; R"=C_2H_5)
XVI (R=OCH_3; R'=CH_3; R"=C_2H_5)

Les structures des produits (XII) ... (XVI) ont été établies à partir des analyses chimiques et spectrales (IR et RMN ^1H).

Les spectres IR des produits (XII) ... (XVI) présentent des bandes d'absorption caractéristiques à 1 725 cm^{-1} ($\nu_{C=O\ ester}$) et à 1 675 cm^{-1} ($\nu_{C=O\ cétonique}$).

Les données les plus édifiantes, nécessaires à la détermination de la structure des produits (XI) ... (XVII), sont celles fournies par les spectres RMN ^1H, ainsi que l'analogie avec les structures des produits (II), (III) et (IV).

On part du fait, prouvé dans le cas des produits (II) et (III) (Fig. 1, [2]), que le proton H_{7a} et le groupement benzoyle se trouvent du même côté du cycle pyrrolique. On a constaté que les spectres RMN ^1H des adduits cycliques (XII) ... (XVI) présentent des signaux similaires pour les protons des cycles tétrahydropyrroliques. Nous avons choisi, pour l'étude minutieuse du spectre RMN ^1H, le produit (XII), qui présente la structure se prêtant au mieux a une interprétation de ce point de vue. On a tenu compte du fait que ce produit est beaucoup plus soluble dans le chloroforme deutérié que les autres hétérocycles (XIII) ... (XVI) et que le signal du groupement CO_2CH_3 n'est pas supperposé aux signaux des protons H_5 et H_6.

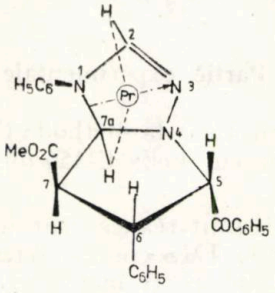
Les protons du cycle pyrrolique du produit (XII) présentent trois signaux : un doublet *A* à $\delta_A = 6{,}4$ ppm avec une constante de couplage de 5,5 Hz, un doublet *B* à $\delta_B = 5{,}8$ ppm ($J = 5{,}7$ Hz) et un multiplet à 4,0 ... 4,3 ppm. Par analogie avec les analyses spectrales des produits (II) et (III)

(Fig. 1), on a attribué ce multiplet aux protons H_6 et H_7. L'analyse de ce multiplet par la technique du découplage du spin, des irradiations du type H_6, $H_7-(H_AH_B)$, montrent que les déplacements chimiques des deux protons sont: $\delta_{H_6}=4,1$ ppm et $\delta_{H_7}=4,2$ ppm ($J_{6,7}=11,2$ Hz). On observe que la valeur de cette constante de couplage est proche de celle ($J_{6,7}=10,2$ Hz) du produit (III) (Fig. 1 *b*).

Pour l'attribution exacte des doublets *A* et *B* nous avons rencontré de grandes difficultés. Par exemple, nous avons essayé d'obtenir l'adduit (XII) deutérié à partir de l'ylure (I) soit sur le proton ylurique, soit dans le cycle triazolique, mais le spectre RMN ^1H de l'adduit (XII) deutérié ne présente pas des intensités des signaux *A* et *B* sensiblement différentes de celles obtenues dans le spectre du produit (XII) nondeutérié.

La seule méthode disponible pour attribuer les doublets *A* et *B* a été celle des déplacements chimiques induits par réactifs de déplacements chimiques (LSR) en uttilisant $Pr(fod)_3$. En suivant la dépendance du spectre en fonction de la concentration du $Pr(fod)_3$ dans la solution de l'adduit (XII), on a constaté que les plus importants déplacements chimiques induits sont ceux qui correspondent au proton H_2 et au doublet *B*, tandis que le doublet *A* n'est que très peu affecté.

Par analogie avec le produit (IV), nous pouvons affirmer que l'ion paramagnétique de praséodyme forme un complexe à proximité de l'atome H_2, c'est-à-dire avec les atomes d'azote N_1 et N_3. La littérature [10], [11] montre que dans les molécules polyfonctionnelles les facteurs qui déterminent la position du complexe sont d'abord le dégagement stérique et puis la basicité. Tenant compte qu'à l'atome d'azote *1* est lié un cycle benzénique, il résulte que la formation du complexe a lieu, très probablement, à l'atome d'azote *3*, tout comme dans des cas analogues [12] et attaque la molécule sous le plan du cycle triazolique :



De cette façon les protons H_2 et H_{7a} sont les plus proches et donc les plus susceptibles d'être déplacés. Par suite, il résulte que le doublet *B* provient du proton H_{7a} tandis que le doublet *A* provient du proton H_5.

Il faut mentionner que la formation d'un complexe de l'ion de praséodyme avec l'atome d'oxygène du groupement benzoyle en position *5* ou l'oxygène C=O estérique du groupement CO_2CH_3 en position *7*, est moins

probable compte tenu que les protons en *ortho* du noyau benzénique et les protons $-CO_2C\underline{H}_3$ présentent des déplacements chimiques induits très réduits.

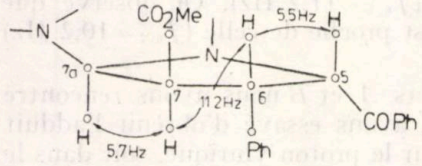


Fig. 3. — Les distributions spatiales des protons du cycle pyrrolidinique dans le produit (XII).

En comparant les valeurs des déplacements chimiques $\delta_{H_{7a}}=5,8$ ppm et $\delta_{H_5}=6,4$ ppm dans le spectre RMN du produit (XII), avec ceux des protons similaires dans le spectre RMN du produit (III) ($\delta_{H_{7a}}=5,8$ ppm et $\delta_{H_5}=6,0$ ppm), il résulte que le proton H_5 du produit (XII) est plus désécranné. Cet aspect peut être expliqué si on admet que le radicale phényle, provenant du cinnamate de méthyle, se trouve dans son voisinage, donc en position *6*. Par analogie à la structure établie pour le produit (III) [2] (Fig. 1 *b*), on peut admettre la géométrie du cycle de type pyrrolique dans le produit (XII) représentée dans la Fig. 3.

La structure établie pour le produit (XII) est aussi valable pour les produits similaires (XIII) ... (XVI).

Conformément à l'analyse spectrale RMN ^1H on peut affirmer que dans la réaction entre les triazolium-phénacylures (I), (V), (VI) et (VII) avec les esters *trans* cinnamiques on retrouve le couplage *trans* entre les protons H_6 et H_7, la réaction ayant un caractère stéréospécifique. En ce qui concerne le problème de la régiochimie lié à ce type de réaction, on constate que les données expérimentales vérifient la conclusion théorique selon laquelle l'atome de carbon C_2 substitué par le radicale phényle du dipolarophile est celui qui se lie au carbanion ylurique.

En conclusion, on peut admettre que les réactions de cycloaddition 3+2 dipolaire entre les systèmes réactants analysés sont *cis*-stéréospecifiques et suivent un sens d'addition dans lequel le carbanion ylurique se lie à l'atome de carbone substitué par le phényle du dipolarophile.

3. Partie expérimentale

Les calculs sont effectués par la méthode CNDO/2 avec le programme QCPE no. 141, sur un ordinateur Felix C-256 du Centre de Calcul de l'Université de Jassy.

Les spectres de RMN ^1H sont réalisés sur un spectromètre JNM-C-60 HL à 60 MHz, en utilisant le TMS comme référence interne. Les spectres IR ont été enregistrés sur un spectromètre Specord-71.

La préparation des sels de cycloimmonium (VIII) ... (X) a été déjà décrite dans des travaux antérieurs [2], [5]. Les cinnamates d'éthyle et de méthyle ont été préparés selon les indications de la littérature [13].

a) *Bromure de N-(p-méthoxy)-phénacyl (p-tolyl)-4 triazolium-1, 2, 4 (XI)*

On dissout 10 mmol de (*p*-tolyl)-4 triazol-1, 2, 4 dans 15 ml chloroforme et 10 mmol de bromure de *p*-méthoxy-phénacyle dans 15 ml de benzène anhydre. On mélange les deux solutions et on abandonne le mélange réactionnel à la température ambiante pendant 24 hr. On filtre le

précipité abondant blanc, on le lave par le chloroforme et on le recristallise dans de l'alcool éthylique anhydre. Cristaux blancs (2,95 g) ; $t_{fus.}$ = 232°C.

Analyse : $C_{18}H_{18}O_2N_3Br$; calculé : N 10,82 ; trouvé : N 10,35%. IR (KBr, cm^{-1}) : $\nu_{C=O}$ = 1 680.

3.1. Méthode générale d'obtention des produits des réaction des triazolium-phénacylures avec les esters *trans* cinnamiques

On suspend 10 mmol de sel de cycloimmonium dans 50 ml de chloroforme et on ajoute 10 mmol d'ester *trans* cinnamique. On laisse tomber goutte à goutte, en agitant continuellement, une solution de 15 ml triéthylamine dans 15 ml de chloroforme. Le mélange réactionnel est agité pendant 1 hr et puis abandonné 48 hr à la température ambiante. On porte à reflux pendant 1/4 hr, on lave la solution organique trois fois à l'eau et on la sèche sur Na_2SO_4 anhydre. On chasse le solvant et on recristallise le résidu dans un mélange chloroforme—méthanol.

b) *Phényl-1 benzoyl-5 phényl-6 carbométhoxy-7 tétrahidropyrrolo-1,2b-triazole-1, 2, 4 (XII)*

On l'obtient par la méthode générale à partir de 10 mmol de sel (VIII) et 10 mmol de cinnamate de méthyle. Cristaux aciculaires jaunes (2 g) ; $t_{fus.}$ = 145°...146°C.

Analyse : $C_{26}H_{23}N_3O_3$, calculé : N 9,88 ; trouvé N 9,45%. IR (KBr, cm^{-1}) : $\nu_{C=O\ ester}$ = = 1 725, $\nu_{C=O\ cétone}$ = 1 675. RMN ($CDCl_3$, δ) : 3,1 ppm, singulet, 3*p* (CO_2CH_3) ; 4,2...4,3 ppm, multiplet, 2*p* (H_6 et H_7) ; 5,75 ppm, doublet, 1*p* (H_5) ; 6,45 ppm, doublet, 1*p* (H_{7a}) ; 7,35 ppm, singulet, 1*p* (H_2) ; 6,9...7,7 ppm, multiplet (15 protons aromatiques).

c) *Phényl-1 benzoyl-5 phényl-6 carbéthoxy-7 tétrahydropyrrolo-1,2b-triazole-1, 2, 4 (XIII)*

On le prépare par la méthode générale à partir de 10 mmol de sel (VIII) et 10 mmol de cinnamate d'éthyle. Cristaux jaunes (2,1 g) ; $t_{fus.}$ = 179°...180°C.

Analyse : $C_{27}H_{25}N_3O_3$, calculé: N 9,56; trouvé N 9,05%. IR (KBr, cm^{-1}) : $\nu_{C=O\ ester}$ = 1 725, $\nu_{C=O\ cétone}$ = 1 675. RMN ($CDCl_3$, δ) : 1,4...1,7 ppm, multiplet, 3*p* ($CO_2CH_2C\underline{H}_3$) ; 3,5...4,0 ppm, multiplet, 2*p* ($CO_2C\underline{H}_2CH_3$) ; 4,2...4,4 ppm, multiplet, 2*p* (H_6 et H_7) ; 5,9 ppm, doublet, 1*p* (H_5) ; 6,5 ppm, doublet, 1*p* (H_{7a}) ; 6,9...8,2 ppm, multiplet (15 protons aromatiques).

d) *Phényl-1(p-nitro)-benzoyl-5 phényl-6 carbéthoxy-7 tétrahydropyrrolo-1,2b-triazole-1, 2, 4 (XIV)*

On l'obtient selon la méthode générale à partir de 10 mmol de sel (IX) et 10 mmol de cinnamate d'éthyle, Cristaux oranges (2,45 g) ; $t_{fus.}$ = 170°...171°C.

Analyse : $C_{27}H_{24}N_4O_5$, calculé : N 11,57 ; trouvé N 11,22%. IR (KBr, cm^{-1}) : $\nu_{C=O\ ester}$ = = 1 725, $\nu_{C=O\ cétone}$ = 1 680. RMN ($CDCl_3$, δ) : 1,4 ppm, triplet, 3*p* ($CO_2CH_2C\underline{H}_3$) ; 3,4 et 3,6 ppm, deux signaux quartets 2*p* ($CO_2C\underline{H}_2CH_3$) ; 4,5...4,6 ppm, multiplet, 2*p* (H_6 et H_7) ; 5,7 ppm, doublet, 1*p* (H_5); 6,35 ppm, doublet, 1*p* (H_{7a}) ; 7,6 et 8,0 ppm, spectre *AA'MM'* provenant des 4*p* aromatiques du fragment $C_6\underline{H}_4—NO_2(p)$; 7,35 ppm, singulet, 1*p* (H_2) ; 7,0...7,5 ppm, multiplet, 10*p* des deux cycles benzéniques nonsubstitués.

e) *p-Tolyl-1 (p-nitro)-benzoyl-5 phényl-6 carbéthoxy-7 tétrahydropyrrolo-1,2b-triazole-1, 2, 4 (XV)*

On le prépare par la méthode générale à partir de 10 mmol de sel (X) et de 10 mmol, de cinnamate d'éthyle. Cristaux beige-nacrés, (1,96 g); $t_{fus.}$ = 176°...177°C.

Analyse: $C_{28}H_{26}N_4O_5$, calculé N 11,24; trouvé N 11,55%. IR (KBr, cm^{-1}) : $\nu_{C=O\ ester}$ = 1 730 $\nu_{C=O\ cétone}$ = 1 685. RMN ($CDCl_3$, δ) : 1,4 ppm, triplet, 3*p* ($CO_2CH_2C\underline{H}_3$) ; 3,4 et 3,6, deux quartets, provenant des 2*p* ($CO_2C\underline{H}_2CH_3$) qui ne sont pas équivalents du point de vue magnétique ; 2,3 ppm, singulet, 3*p* ($—C_6H_4—C\underline{H}_3$) ; 4,5...4,6 ppm, multiplet, 2*p* (H_6 et H_7) ; 5,65 ppm, doublet, 1*p* (H_5) ; 6,3 ppm, doublet, 1*p* (H_{7a}) ; 7,6 et 8,0 ppm, spectre *AA'MM'* provenant des 4*p* aromatiques du fragment ($C_6H_4—NO_2(p)$) ; 6,7...7,3 ppm, multiplet, 9*p* aromatiques.

f) *p-Tolyl-1 (p-méthoxy)-benzoyl-5 phényl-6 carbéthoxy-7 tétrahydropyrrolo-1,2b-triazole-1, 2, 4 (XVI)*

On le pépare par la méthode générale à partir de 10 mmol de sel (XI) et de 10 mmol de cinnamate d'éthyle. Cristaux jauné-pailles, (2,05 g) ; $t_{fus.}$ = 148°...149°C.

Analyse : $C_{29}H_{29}N_3O_4$, calculé N 8,69 ; trouvé N 8,38%. IR (KBr, cm^{-1}) : $\nu_{C=O\ ester}$ = = 1 720, $\nu_{C=O\ cétone}$ = 1 660. RMN ($CDCl_3$, δ) : 1,4 ppm, triplet, 3*p* ($CO_2CH_2\underline{CH_3}$); 3,35 et 3,55 ppm, deux signaux quartets provenant des 2*p* ($CO_2\underline{CH_2}CH_3$) nonéquivalents ; 2,25 ppm, singulet, 3*p* ($C_6H_4-\underline{CH_3}$) ; 3,75 ppm, singulet, 3*p* ($C_6H_4-O\underline{CH_3}$)); 4,5...4,6 ppm, 2*p* (H_6 et H_7) ; 5,65 ppm doublet, 1*p* (H_5) ; 6,3 ppm, doublet, 1*p* (H_{7a}) ; 6,8 et 7,0 ppm, spectre des 4*p* aromatiques du fragment $-(C_6\underline{H_4}-CH_3$ (*p*) ; 6,6 ppm et 7,5 ppm, spectre des 4*p* aromatiques du fragment $-C_6\underline{H_4}-OCH_3$ (*p*) ; 7,2 ppm, multiplet des 5*p* aromatiques $-C_6H_5$.

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1, 2, 4-TRIAZOLIU-ILIDE

IX. Reacţia de cicloadiţie 3 + 2 dipolară între triazoliu-fenacilide şi esterii cinamici

(Rezumat)

In continuarea cercetărilor privind reactivitatea triazoliu-ilidelor, s-au studiat reacţiile de cicloadiţie ale ilidelor (I), (V), (VI) şi (VII) la cinamaţii de etil şi de metil. S-au obţinut cicloaducţii (XII) — (VI) în care carbanionul ilidic este legat de atomul de carbon substituit prin grupa fenil a dipolarofilului.

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SYNTHESE UND POLYMERISIERUNG EINIGER NEUEN CHLOROFORMYLIERTEN VINYLVERBINDUNGEN

VON

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1. Einleitung

Da sich die Polymere mit reaktiven Gruppen auf der makromolekularen Kette zu polymer—analogen Reaktionen eignen, bieten sie ein besonderes theoretisches und praktisches Interesse dar.

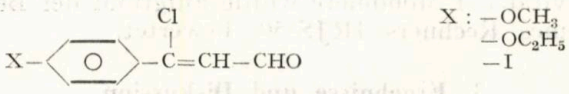
Solche Polymere wurden auch durch die Polymerisierung oder Kopolymerisierung der chloroformylierten Vinylverbindungen erhalten [1], [2].

In vorherigen Arbeiten wurde der Einfluß einiger Substituenten I. Grades (CH_3, $CH(CH_3)_2$, Cl, Br) und II. Grades (NO_2) auf die Reaktivität des α-Chlor-β-Formylstyrens in Polymerisationsreaktion dargestellt [3]...[5].

In der vorliegenden Arbeit wird die Synthese und die Charakterisierung einiger neuen chloroformylierten *p*-substituierten Vinylverbindungen dargestellt, sowie einige Versuche hinsichtlich ihrer thermischen Polymerisierung zwecks Beurteilung des Einflußes des Substituenten auf die Reaktivität des Monomers bei der Polymerisierung.

2. Experimenteller Teil

a) *Die Monomere* vom Typ :



wurden aus dem entsprechend substituierten Acetophenon synthetisiert durch die Reaktion mit dem Komplex Vielsmeier ($DMF/POCl_3$).

b) *p-Methoxy-und p-Äthoxyacetophenon* wurden durch die Acylierung des Phenoläthers mit Essigsäureanhydrid in Gegenwart von $AlCl_3$ dargestellt, mit der Bestimmung der optimalen Reaktionsparameter. Die Ausbeute ist gut (75 ... 80%) bei der Reaktionstemperatur von 80°C und molarem Verhältnis Äther/Katalysator von 1 : 1,6; als Lösungsmittel diente das Substrat.

c) *p-Jodacetophenon* wurde durch die Behandlung des Diazoniumsalzes des *p*-Aminoacetophenons mit einer Kaliumjodid-Lösung synthetisiert.

d) *Die chloroformylierten Vinylverbindungen* wurden gemäß der in der Literatur [6] ... [8] beschriebenen Methode erhalten. Die optimalen Reaktionsparameter und einige Merkmale sind in der Tabelle 1 wiedergegeben.

Tabelle 1

Die Reaktionsparameter und die Merkmale der Monomere

Nr.	Vinylverbindung	Keton/ DMF	Reaktiv Vielsmeier $POCl_3$/ DMF	Temperatur °C	Reak. Zeit Min.	Aspekt	Schm. punkt °C	Löslichkeit
1	α-Chlor-β-Formyl-*p*-Methoxystyren	20 mM/ 35 ml	9/30 ml	0 70 20	15 120 90	Weissgelbe Nadeln	50	Grosteil organ. Lösn.
2	α-Chlor-β-Formyl-*p*-Äthoxystyren	10 mM/ 30 ml	5/20 ml	0 75 ... 80 20	30 120 90	Gelbbraunes Öl	—	Grosteil organ. Lösn.
3	α-Chlor-β-Formyl-*p*-Jodstyren	10 mM/ 15 ml	5/15 ml	0 50 ... 55 20	30 120 90	Weisse Flocken	94	Grosteil organ. Lösn.

Die Polymerisation wurde in inerter Atmosphäre in verschlossenen Phiolen durchgeführt.

Die IR Spektren, in KBr Tabletten, wurden mittels eines Spektrophotometers UR-20 aufgezeichnet, die RMN Spektren mit einem Apparat vom Typ JEOL, bei 25°C, unter Verwendung von $CDCl_3$ als Lösungsmittel und TMS als Referenzsystem.

Die thermische Stabilität wurde anhand der mit einem Derivatograph Typ MOM Budapest, J. Paulik—F. Paulik—L. Erdey, inregistrierten Thermogramme beurteilt.

Die Reaktivität der Monomere wurde aufgrund der Bestimmung der HMO, mittels eines Rechners IRJS-50, bewertet.

3. Ergebnisse und Diskussion

3.1. Die Struktur und Reaktivität der Monomere

Die Vinyl-Monomere wurden anhand der Elementar-, der Spektral- (IR und RMN) und der Thermodifferential-Analyse charakterisiert.

Die IR Spektren weisen die characteristischen Bände der funktionellen Gruppen und des aromatischen Rings auf. Die Wertigkeitsvibration der Karbonyl-Gruppe tritt bei 1 650 cm^{-1} in den Spektren aller Monomere auf. Die charakteristische Absorption der äthylenischen Doppelbindung und des am ungesättigten Karbonyl fixierten Halogens überlagert sich mit jener des aromatischen Rings. Das Absorbtionsband bei 1 025 cm^{-1} rührt von der ätherischen Verbindung C—O—C her.

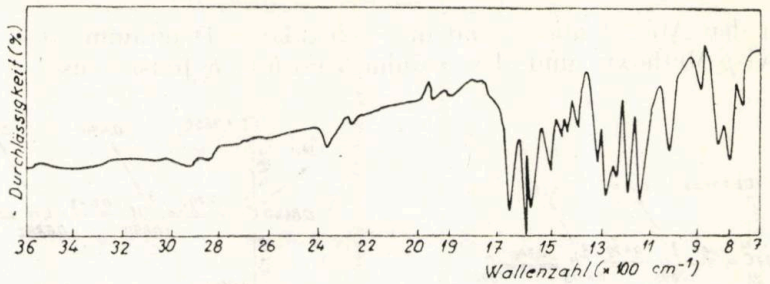
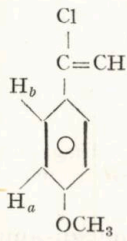
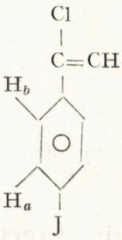


Abb. 1. — Das IR Spektrum des α-Chlor-β-Formyl-*p*-Methoxystyrens.

Die chemischen Verschiebungen *der RMN-Spektren* bestätigen die Struktur der Monomere :



	δ, [ppm]
CHO	10,33
=CH	6,58
H_a	7,69
H_b	6,89
CH_3	3,86



J

	δ, [ppm]
CHO	10,41
=CH	6,55
H_a	7,70
H_b	7,32

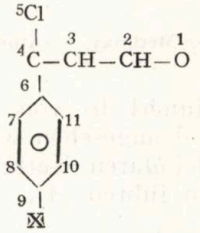
Die Thermodifferentielle Analyse des α-Chlor-β-Formyl-*p*-Methoxy- und des α-Chlor-β-Formyl-*p*-Jodstyrens zeigt eine Zerlegung in zwei Etappen an ; beide Monomere sind bis 100°C stabil.

Tabelle 2

Abhängigkeit des Gewichtsabfalls von der Temperatur

Monomer	Temperatur-intervall °C	Gewichts-abfall %
α-Chlor-β-Formyl-*p*-Methoxystyren	100 ... 300 300 ... 700	61 100
α-Chlor-β-Formyl-*p*-Jodstyren	100 ... 370 370 ... 700	73,3 100

Um den Einfluß **des Subs**tituenten aus der Stellung *para* auf die Reaktivität der **Monomere** abzuschätzen, wurde die *Methode LCAO — MO* angewendet. Bei der Berechnung wurden folgende Parameter angewendet [11], [12] :



XI

$\alpha_{Cl}=\alpha+2{,}5\,\beta$, $\alpha_J=\alpha+1{,}2\,\beta$, $\alpha_O=\alpha+\beta$, $\alpha_O=\alpha+2\,\beta$, $\alpha_{C\equiv H_3}=\alpha+2\,\beta$;

$\beta_{C-C\equiv H_2}=0{,}7\,\beta$, $\beta_{C-Cl}=0{,}6\,\beta$, $\beta_{C=O}=\beta$, $\beta_{C-J}=0{,}3\,\beta$, $\beta_{C-O}=0{,}8\,\beta$, $\beta_{1,2}=\beta_{3,4}=1{,}1\,\beta$, $\beta_{2,3}=0{,}9\,\beta$.

In den Abb. 2 und 3 sind die molekularen Diagramme des α-Chlor-β-Formyl-*p*-Methoxy- und des α-Chlor-β-Formyl-*p*-Jodstyrens.

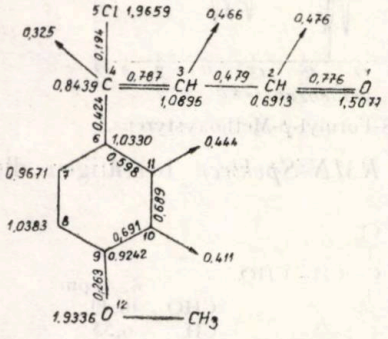


Abb. 2. — Das Molekular-Diagramm des α-Clor-β-Formyl-*p*-Methoxystyrens.

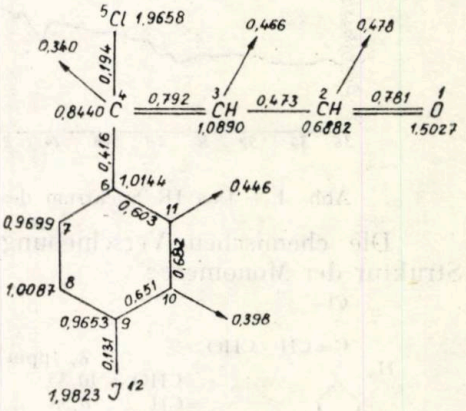


Abb. 3. — Das Molekular-Diagramm des α-Chlor-β-Formyl-*p*-Jodstyrens.

In Tabelle 3 sind die Ergebnisse der HMO-Berechnung zusammengefaßt.

Tabelle 3

Molekulare Merkmale der Monomere

Monomer	E_{II} β	LUMO β	L_3^0	F_{mean} C_3-C_4
α-Chlor-β-Formyl-*p*-Methoxystyren	23,772	0,407	2,313	0,396
α-Chlor-β-Formyl-*p*-Jodstyren	22,003	0,389	2,307	0,403

LUMO — Lowest Unoccupied MO ; L^0 — Radicalic Localization Energy ; F_{mean} — Mean Free Valence.

Falls die thermische Polymerisation radikalisch verläuft, erlauben es die Werte aus Tabelle 3 und jene aus den Molekular-Diagrammen zu behaupten, daß das *p*-jodierte Monomer reaktionsfähiger ist als jenes *p*-methoxylierte. Bei beiden Verbindungen beginnt der radikalische Angriff beim C_3-Atom, (F_3, F_4 ; Abb. 2 und 3).

3.2. Thermische Polymerisation des α-Chlor-β-Formyl-*p*-Methoxy, -*p*-Äthoxy- und -*p*-Jodstyrens

Die thermische Polymerisation wurde innerhalb von 10 Stunden durchgeführt, eine Reaktionszeit die als optimal angesehen wurde, da bei deren Verlängerung Spaltungen der makromolekularen Kette stattfinden, die zur Bildung von Trimeren oder Tetrameren führen [4].

Die Daten hinsichtlich dem Einfluß der Temperatur auf die Ausbeute sind in Tabelle 4 enthalten.

Tabelle 4

Der Einfluss der Temperatur auf die Ausbeute

Polymer	Reaktionstemperatur °C	Umsatz %	Schmelzpunkt °C
A	150	10,5*)	162
		7	210
A	180	9*)	165
		17	220
A	200	—*)	
		36,7	220
B	150	—	—
B	180	15*)	176
		18,5	235
B	200	—*)	—
		34	235
C	150	—	—
C	180	—*)	—
		25,5	256
C	200	—*)	—
		47,7	256

A — Polymer erhalten durch die Polymerisierung des α-Chlor-β-Formyl-*p*-Methoxystyrens;

B — Polymer erhalten durch die Polymerisierung des α-Chlor-β-Formyl-*p*-Äthoxystyrens;

C — Polymer erhalten durch die Polymerisierung des α-Chlor-β-Formyl-*p*-Jodstyrens;

*) lösliche Fraktion.

Man stellt fest, daß in allen Fällen der Umsatz mit der Reaktionstemperatur steigt, die größten Werte wurden beim *p*-jodierten Monomer verzeichnet. Die lösliche Fraktion nimmt mit steigender Temperatur ab, bei 200°C erhält man nur unlösliche Polymere.

Es wurde bewiesen, daß die löslichen Fraktionen Oligomere sind, deren Polymerisationsgrad zwischen 3 und 10 schwankt, und die in fast allen organischen Lösungsmitteln, mit Ausnahme des Methyl- und Äthylalkohols, löslich sind.

3.3. Molekularstruktur der Polymere

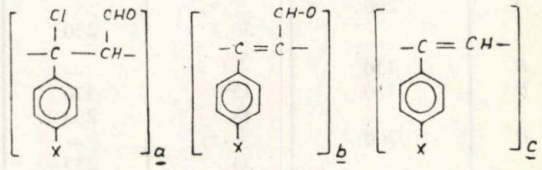
Die Struktur der Polymere wurde anhand der Elementaranalyse und der IR Spektren aufgeklärt. In allen Fällen sind die bei verschiedenen Temperaturen erhaltenen IR Spektren der Polymere identisch und weisen alle charakteristischen Bände der Monomere auf, jedoch ist ihre Intensität geringer.

Die Polymerisation ist thermisch initiiert und verläuft gemäß dem radikalischen Mechanismus, der in den vorherigen Arbeiten angegeben wurde [3] ... [5].

Die Ergebnisse der Elementar- und Spektralanalyse weisen auf eine Dehydrohalogenierung und Dehaloformylierung des Polymers oder des Monomers hin. Während dieses komplexen Prozeßes können sich auch azetylenische Monomere bilden, die mit Vinylmonomeren kopolymerisieren [4].

Diese Ergebnisse stimmen mit den Literaturangaben hinsichtlich der thermischen Dehydrohalogenierung des Polyvinylchlorids [13] oder des Polyphenilenbromäthens [14] überein, die einen durch die Spaltung der Bindung C-Halogen initiierten radikalischen Prozeß voraussetzt. Korschak [15] und Pauschkin [1] haben, ebenfalls, eine Dehydrohalogenierung bei der Polymerisation des 1-Chlor-2-Formyl-Vinylferrocens beobachtet.

Die löslichen Fraktionen sind lineare Kopolymere dessen Struktur im Abb. 4 repräsentiert sind.



Polymer *A*, X = $-OCH_3$;
Polymer *B*, X = $-OC_2H_5$;
Polymer *C*, X = $-I$

Abb. 4. — Die Molekularstruktur der Polymere.

4. Schlussfolgerungen

1. Es wird die Synthese drei neuer *p*-substituierten Vinylverbindungen dargestellt: α-Chlor-β-Formyl-*p*-Methoxy, -*p*-Äthoxy- und -*p*-Jod-styren, unter Festlegung der optimalen Reaktionsparameter.

2. Die Monomere wurden durch Elementar-, Spektral- und Thermodifferential-Analyse charakterisiert.

3. Es wurden LCAO—MO berechnet, anhand derer die Reaktivität der Monomere während der Polymerisation bewertet wurde.

4. Der Umsatz steigt mit der Temperatur bei beiden Monomeren.

5. Die Korrelation der Daten der Elementaranalyse mit jenen der Spektralanalyse führt zur Schlußfolgerung, daß die löslichen Produkte Kopolymere linearer Struktur sind, deren Polymerisationsgrad zwischen 3 und 10 variiert, während die unlöslichen Verbindungen eine verzweigte Struktur aufweisen.

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makromolekulare Chemie und Technologie

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SINTEZA ȘI POLIMERIZAREA UNOR NOI DERIVAȚI VINILICI CLOROFORMILAȚI

(Rezumat)

Se studiază sinteza și polimerizarea termică a unor derivați vinilici *p*-substituiți. Influența substituentului asupra reactivității monomerilor în reacția de polimerizare termică s-a apreciat pe baza calculelor HMO, cît și pe baza datelor experimentale.

Prin polimerizarea termică s-au obținut fracții solubile cu structură liniară și fracții insolubile cu structură ramifi cată.

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C.D. 547.861.1

SYNTHÈSE DE QUELQUES NOUVEAUX DÉRIVÉS PYRIDAZINIQUES CAPABLES À INFLUENCER LE SYSTÈME NERVEUX CENTRAL (I)

PAR

IOANA CIOCOIU, ȘT. CILIANU, AL. CÎRSTEA, RALUCA BOZGA, MARIA CAPROȘU, EUGENIA ȘTEFĂNESCU et MAGDA PETROVANU

1. Introduction

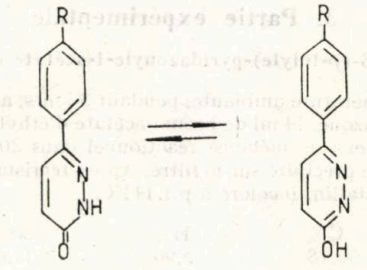
Dans une série de recherches antérieures [1]...[12] on a synthétisé un nombre assez grand de nouveaux dérivés pyridaziniques et phtalaziniques en mettant en évidence une série de propriétés physiologiques importantes de ces produits parmi lesquelles on peut citer : des propriétés antihypertensives [1]...[5], antibactériennes, antiinflamatoires et fungistatiques [6]...[12].

Tenant compte du fait que la littérature [13] indique aussi des propriétés anticonvulsivantes, sédatives, de quelques produits pyridaziniques, nous avons commencé des recherches dans le but de dépister de nouvelles structures pyridaziniques on phtalaziniques possédant une éventuelle activité sur le système nerveux central.

Dans ce qui suit on présente une série de nouveaux esters appartenant à la classe des 3-aryl-pyridazones.

2. Résultats et discussions

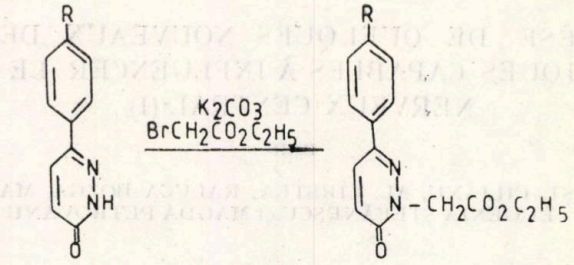
Pour la synthèse des 3-aryl-pyridazones du type (1) on a utilisé une méthode indiquée dans la littérature [14] qu'on a modifié en fonction de l'hydrocarbure utilisé.



(1)

R = -CH3 , -CH(CH3)2 , Cl

Dans le but d'obtenir des produits possédant une éventuelle activité psychotrope, au cours de nos recherches nous avons synthétisé, dans une première étape, des 3(-aryl) pyridazonyle-acétates d'éthyle du type (2, R= $=CH_3$, $-CH\begin{matrix}-CH_3\\-CH_3\end{matrix}$, Cl) en traitant les 3-aryle-pyridazones (1) avec du bromoacétate d'éthyle en milieu de DMF et en présence de K_2CO_3 anhydre.



(2)

$R = -CH_3$; $-CH\begin{matrix}-CH_3\\-CH_3\end{matrix}$; Cl

La méthode que nous avons utilisée (Brevet nr. *75 836* (1980)) nous a été suggérée par la mobilité de l'hydrogène attaché á l'atome d'azote en position *1*.

Les trois esters nouveaux du type 2($R=CH_3$, $-CH\begin{matrix}-CH_3\\-CH_3\end{matrix}$, Cl) ont été caractérisés par voies chimique et spectrale.

Les produits obtenus ont été testé à l'Institut de Recherches Chimico-Pharmaceutiques de Bucarest. On a constaté que les trois produits manifestent une activité psychotrope de type sédatif, tranquilisant, ayant aussi des propriétes hypothermisantes et anticonvulsivantes.

3. Partie expérimentale

3.1. Le 3-(*p*-tolyle)-pyridazonyle-1-acétate d'éthyle

On abandonne à la température ambiante, pendant 3 jours, avec agitation occasionelle, un mélange de 20 g *p*-tolyle-pyridazone, 14 ml de bromo-acétate d'éthyle, 30 g de K_2CO_3 dans 120 ml de diméthyleformamide. On verse le mélange réactionnel dans 200 ml d'eau (pH = 8...9), on filtre et on lave avec de l'eau le précipité sur le filtre. Après recristallisation dans l'alcool éthylique on obtient un produit cristallin, incolore à p.f. 141°C.

Analyse : $C_{15}H_{16}O_3N_2$	C%	H%	N%
Calculé :	66,18	5,90	17,64
Trouvé :	66,00	5,70	17,44

Spectre IR (KBr) : 1 715 $\nu_{C=O\,(est)}$; 1 587 $\nu_{C=N}$; 1 203, 1 232 ν_{C-OC} ; 820 $\nu_{\text{ø}-H}$; 2 875 ν_{C-H} ; 2 930 $\nu_{\text{ø}-H}$.

3.2. Le 3-(*p*.cumyle)-pyridazonyle-1-acétate d'éthyle

On abandonne pendant 2...3 jours, à la température ambiante, un mélange de 22 g *p*. cumyl-pyridazone, 14 ml bromo-acétate d'éthyle, 20 g K_2CO_3 dans 120 ml DMF. Agitation occasionelle. On verse ensuite le mélange réactionnel dans de l'eau glacée. On filtre et on lave le précipité sur le filtre avec de l'eau. Après recristallisation dans de l'alcool éthylique on obtient des cristaux incolores à p.f. 84°C.

Analyse : $C_{17}H_{20}N_2O_3$	C%	H%	N%
Calculé :	68,00	6,66	9,33
Trouvé :	67,80	6,54	10,00

3.3. Le 3-*p*.(chloro-phényl))-pyridazonyle-1-acétate d'éthyle

On abandonne pendant 2...3 jours, à la température ambiante, un mélange de 20 g *p*.chloro-phényle-pyridazone, 1,35 ml de bromoacétate d'éthyle et 10 g K_2CO_3 dans 200 ml de diméthylformamide. On verse ensuite le mélange réactionnel dans 200 ml d'eau (pH = 8...9), on filtre et on lave le précipité à l'eau. Après recristalisation dans l'étanol on obtient un produit cristallin incolore à 163°C.

Analyse : $C_{14}H_{13}N_2O_3$	C%	H%	N%
Calculé :	57,43	4,44	10,80
Trouvé :	56,87 ; 57,20	4,23 ; 4,45	10,50

4. Recherches pharmacodynamiques

Pour le teste pharmacodynamique on a choisi les produits suivants : S_1 — 3-*p* (tolyle) pyridazonyle-1-éthyle acétate ; S_2 — 3-*p* (cumyle) pyridazonyle-1-éthyle acétate ; S_3 — 3-*p* (chlorophényle) pyridazonyle-1-éthyl acétate.

Tableau 1

Produit	Voie d'administration	Tolérance toxique	DL_{50}
S_1	i.p.	2 000 mg/kg Mortalité 0/24 h	—
S_2	i.p.	—	1 803 mg/kg
S_3	i.p.	1 000 mg/kg Mortalité 0/24 h	—

Les résultats obtenus sont donnés dans le Tableau 1.

On peut constater une toxicité réduite des épreuves, en général ; on fait une remarque spéciale pour les produits S_1 et S_3, supportés par les animaux d'expérience en dose de 2 g respectivement 1 g administrés i.p. avec une mortalité nulle pendant 24 h. Les substances sont insolubles dans de l'eau distillée mais peuvent former de bonnes suspensions dans le même véhicule.

4.1. Le profile pharmacodynamique par l'examen général neurologique

L'administration intrapéritonéale (i.p.) des substances testées en dose de 100 et 200 mg/kg à des souris mâles ayant un poids de 18 ... 20 g provoque un sommeil profond sans signes d'excitation centrale ou périphérique. Le

sommeil dure en moyenne 3 h et s'installe 1/2 h après l'injection i.p. du produit. Après 24 h les animaux récupèrent le comportement normal (ils mangent et bougent, mortalité zéro). Action prédominante sédative.

4.2. Activité sédative—neuroléptique

Cette activité a été déterminée en utilisant les testes suivants: a) le teste de redressement; b) le teste des réflexes d'investigation; c) l'épreuve de l'effort ; d) l'action analgétique ; e) le teste de l'observation de l'influence sur les mouvements spontanés, f) l'action hypothermisante.

a) *Le teste de redressement*

On sélectionne, du point de vue des réflexes stakinétiques, des souris mâles ayant un poids de 18 ... 20 g. On ne retient pour l'expérience que les animaux possédant des réflexes normaux (se redressant en maximum 5 s).

On a administré au lot des animaux sélectionnés le produit à tester (10 animaux chaque lot), i.p., en observant le redressement et le maintien sur la barre à 30; 60 et 120 min. On peut constater la présence d'une action de type sédatif chez les produits étudiés. Les résultats sont présentés dans le Tableau 2.

Tableau 2

Substance	Dose administrée	Efficacité, [%]			Moyenne de l'efficacité
S_1	200 mg/kg i.p.	80	70	60	70,0
S_2	200 mg/kg i.p.	60	70	70	66,6
S_3	200 mg/kg i.p.	50	30	70	50,0

b) *Le teste du réflexe d'investigation*

On a utilisé des souris mâles ayant un poids de 18 ... 20 g, répartis en lots de 10 animaux.

On utilise une plaque de bois mélaminé (40 cm × 40 cm) possédant 16 trous avec un diamètre de 2,5 cm située à une hauteur de 60 cm à partir du sol. Pour chaque lot on note une heure avant l'administration du produit, pendant 5 min., chaque minute pour chaque animal, combien de fois il introduit la tête dans le trou jusqu'au niveau de la marge supérieure de l'oreille.

L'injection i.p. des produits étudiés a été significative pour le réflexe de redressement, les résultats plédant pour leur action sédative. On détermine la moyenne des résultats pour chaque animal, pour chaque minute, ainsi que la moyenne pour les 5 min., ce qui constitue le moment initial. Les mêmes données sont enregistrées une heure après l'administration i.p. des produits.

c) *L'épreuve de la nage (d'effort)*

Les lots de 10 animaux pris en considération (souris mâles ayant un poids de 18 ... 20 g) sont soumis à la nage dans un bassin avec de l'eau à une température constante de 22°C. On note pendant 3 jours le temps

Tableau 3

Produit	Dose administrée	Efficacité, % réduction
S_1	200 mg/kg i.p.	115
S_2	200 mg/kg i.p.	117
S_3	200 mg/kg i.p.	83,1

écoulé jusqu'à l'apparition de la fatigue, on effectue la moyenne des trois jours (le témoin du lot), ensuite on note le temps de nage pour chaque animal à une heure et deux heures après l'administration des produits, ainsi qu'à l'administration d'un ml d'eau distillée au lot des témoins. On peut constater, en analysant les résultats, que, en général, l'administration des produits n'a pas modifié d'une manière significative le temps de nage par rapport au témoin, l'action générale étant prédominante de type sédatif.

Les résultats obtenus sont présentés dans le tableau 4.

Tableau 4

Produit	Dose administrée	Efficacité, [%], par rapport au témoin		Moyenne
		1 h	2 h	
Eau distillée	1 ml i.p.	0,4	0,6	0,5
S_1	200 mg/kg i.p.	1,8	1,2	1,5
S_2	200 mg/kg i.p.	24	4,3	14,5
S_3	200 mg/kg i.p.	11,2	28	19,6

d) *Action analgétique*

On a utilisé la méthode d'enregistrement de l'apparition du temps de réaction (saut des animaux testés, souris mâls ayant chacun un poids d'environ 18 ... 20 g) posés sur une plaque chauffée à 60°C. On a constitué six lots de 10 animaux chacun, pour chaque produit en utilisant pour le calcul la formule Morozzi-Malone.

On note le temps de réaction (TR) de chaque animal à part. S'il ne manifeste aucune réaction en 45 s on l'enlève de la cuve et on note TR = = max = 45 s.

On exprime l'action analgétique à l'aide de la relation :

$$\text{Action analgétique} = \frac{TR_x - TR_0}{45 - TR_0} \cdot 100, \ [\%],$$

où : TR_x représente le temps de réaction chez les lots traités ; TR_0 — temps de réaction chez le lot témoin ; 45 — constante.

e) *Mouvements spontanés*

Pour l'étude de l'activité motrice (mouvements spontanés) on a utilisé un appareil transistorisé qui enregistre, à l'aide d'un compteur, les impulsions provenues à partir de deux photodiodes placées dans un espace dans lequel les animaux bougent librement. On enregistre pendant 1 min. les

Tableau 5

Produit	Dose administrée	Effet, %
S_1	200 mg/kg i.p.	43,5
S_2	200 mg/kg i.p.	40,3
S_3	200 mg/kg i.p.	70,7

mouvements de l'animal soumis à l'expérience (souris mâles, 18 ... 20 g) en poursuivant les mêmes mouvements après 1 h et 2 h après l'injection i.p. des produits.

On peut constater, si on analyse les données résultées, une action de retardement des mouvements spontanés qui s'installe 1/2 h après l'administration et se maintient à 1 et 2 h.

L'examen objectif du comportement des animaux d'expérience conduit à la conclusion qu'on se trouve devant une action de type sédatif. Les résultates sont inscrits au Tableau 6.

Tableau 6

Produit	Dose administrée	Efficacité, [% réduction]			Moyenne
		1/2 h	1 h	2 h	
S_1	200 mg/kg i.p.	34	41,3	57,2	44,16
S_2	200 mg/kg i.p.	25	6,9	45	25,63
S_3	200 mg/kg i.p.	51,5	36,7	58,4	48,8

f) *Action hypothermisante*

À l'aide d'un thermocouple on a poursuivi l'action de diminution de la température par suite de l'administration i.p. des produits testés, chez des souris mâles ayant un poids de 18 ... 20 g.

On a mesuré la température souslinguale après 1/2 h, 1 h et 2 h.

Les résultates montrent une diminution modérée de la température, qui se manifeste surtout pour les produits S_1 et S_3.

Tableau 7

Produit	Dose administrée	Action par rapport à la température normale, [°C] 1/2 h, 1 h et 2 h
S_1	200 mg/kg i.p.	— 1,73
S_2	200 mg/kg i.p.	— 0,7
S_3	200 mg/kg i.p.	→ 1,73

4.3. Action anticonvulsive

On utilise des lots de 10 souris mâles de 18 ... 20 g, auquels on administre du Pentétrazol en doses de 100 mg/kg s.c. Les produits, soumis au teste sont injectés par voie i.p. 60 min. avant l'administration du Pentétrazol. On observe le caractère des convulsions, le moment de leur apparition tant au lot témoin traité au Pentétrazol qu'aux lots qui ont reçu les produits à tester.

Les résultats sont présentes dans le tableau 8.

Tableau 8

Produit	Convulsions clotoniques	Convulsions clotoniques	Moment d'apparition des convulsions secondaires	Mortalité ; moment d'apparition sec.	Mortalité %
Pentétrazol	60	50	298,5	143,5	10
S_1	40	20	321	210	10
Pentétrazol	30	100	201,1	179,0	20
S_2	10	60	247,25	40,5	10
S_3	20	60	294,75	522,0	40

Le produit S_1 est le plus actif, suivi par les produits S_3 et S_2.

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SINTEZA UNOR NOI DERIVAŢI PIRIDAZINICI CU ACŢIUNE ASUPRA SISTEMULUI NERVOS CENTRAL

(Rezumat)

Au fost sintetizaţi trei noi 3-(aril)-piridazonil-acetaţi de etil care au fost testaţi la I.C.C.F., Bucureşti. S-a constatat că aceşti produşi manifestă o activitate psihotropă de tip sedativ, tranchilizantă, avînd şi proprietăţi hipotermizante şi anticonvulsivante.

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C.D. 535.338 : 547.466

ÉTUDE DU SPECTRE INFRAROUGE DE LA 3,3'-THIODIALANINE (*L*-LANTHIONINE)

PAR

SAVEL IFRIM et V. MACOVEI

1. Introduction

L'étude des spectres en infrarouge des amino- et thioaminoacides présente une importance particulière pour l'établissement de la structure et également pour la compréhension du comportement des ces combinaisons. Les aminoacides ont fait l'objet de nombreuses recherches en infrarouge (IR), ainsi comme indique S t e g e r et ses collaborateurs [1], S a l i m o v et ses collaborateurs [2]. (On peut voir aussi la littérature indiquée dans ces travaux).

Au contraire, les thioaminoacides, ainsi comme on a signalé antérieurement [3], sont très peu étudiés par la spectroscopie IR, bien que l'intérêt pour leur comportement biologique augmente sans cesse. Probablement la *L*-lanthionine, isolée et synthétisée assez tard [4], n'a fait jamais l'objet des recherches en IR.

La lanthionine a été isolée d'hydrolysats de la laine et elle est le seul acide aminique de la kératine déterminant l'apparition des liaisons transversales thioéthériques, mettant ensemble deux chaînes polypeptidiques. Le fait que la lanthionine n'a pas été étudiée jusqu'au présent par la spectroscopie en IR peut être expliqué si l'on tient compte que ce composé devrait présenter un spectre très proche de celui de l'alanine [5], [6]. Pourtant, la présensence de l'atome de soufre et la possibilité de l'orientation spatiale différente des deux restes d'alanine liés à l'atome de soufre, doit particulariser le spectre en IR de la 3,3'-thiodialanine. Ces considérations ont déterminé l'étude du spectre en IR de cet acide aminique.

2. Partie expérimentale

En utilisant de la *L*-lanthionine parfaitement pure, procurée de la R.F. Allemagne, sans une autre purification et également la forme deutérisée à l'atome d'azote du produit, on a obtenu les spectres par la technique du pastillage en bromure de potassium (0,240 mg substance en 0,2162 g bromure de potassium) et sous forme de suspension en nuyol. Pour éviter l'humidité atmosphérique, qui influence profondément les spectres en IR des aminoacides, tous les matériaux ont été gardés pendant 48 h dans un box de séchage [7], par lequel on a circulé de l'azote sèche, à la température de 25°C. Les préparations pour l'enregistrement ont été effectuées dans le

même box. L'échange isotopique des hydrogènes de l'azote a été obtenu de la même manière que dans les cas précédentes [7], [8]. Pour l'enregistrement des spectres on a utilisé les appareils décrits antérieurement [3], [7], [8].

3. Résultats et discussions

Les spectres d'absorption en IR de la 3,3'-thiodialanine sont présentés dans la Fig. 1 et pour la forme deutérisée à l'azote dans la Fig. 2 ; les nombres d'onde des maximums des absorptions correspondantes sont indiqués dans le Tableau 1. L'attribution des bandes se fait tenant compte de cinq facteurs à savoir :

1. La structure dipôlaire de l'acide [2], [9], [10], confirmée par l'absence des bandes approchées de 1 700 cm^{-1} [11], [12].
2. La deutérisation, qui a favorisé l'attribution des bandes du groupement $-NH_3^+$.
3. Les attributions précédentes se trouvent dans la littérature [1], [2], [5], [6], [8], [13].
4. Les calculs des bandes pour l'alanine et la glycine, qui confirment les données expérimentales [6], [14]...[17].
5. L'observation [2] que dans le domaine 770 ... 650 cm^{-1} le groupement carboxilique donne des bandes d'intensité moyenne ou plus grandes que la moyenne, l'intensité étant utilisée aussi elle même comme facteur pour l'attribution des bandes.

Ainsi qu'on s'y attendait le spectre de la 3,3'-thiodialanine est différent de celui de la l-alanine [6] et également de celui de la d,l-alanine [5] n'ayant pas des absorptions contournées au-dessus de 3 000 cm^{-1} et en présentant une bande d'intensité moyenne approximativement à 1 258 cm^{-1}, bande qui n'apparaît pas dans les spectres mentionnés [5], [6]. Les autres bandes sont seulement peu déplacées vers les nombres d'onde petits, ce qui est explicable par la présence de l'atome lourd de soufre dans le squelette moléculaire.

Ainsi comme indique la Fig. 1 et le Tableau 1, dans la bande large, dont le maximum principal se trouve approximativement à 2 922 cm^{-1} et qui présente une structure complexe vers la partie des nombres d'onde petits, sur les vibrations d'extension antisymétrique et symétrique des groupements $-CH_2-$ et un peu moins des groupements $=CH-$, se superposent les vibrations antisymétriques, dégénerée et symétrique du groupemment $-NH_3^+$, résultats qui sont évidents au déplacement des vibrations du groupement $-ND_3^+$, après deutérisation.

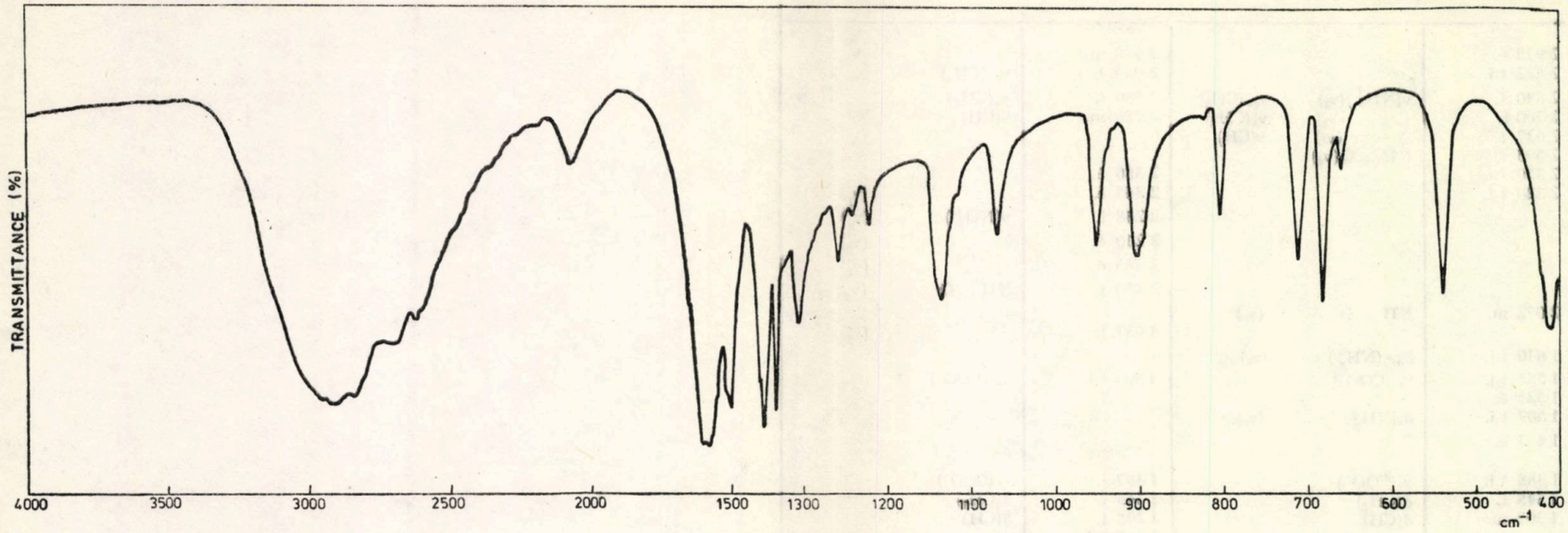
La structure du spectre dans le domaine 6,25 μ est complexe, en se superposant la bande des vibrations de déformation antisymétriques dégénerées $\delta_{as}e$ $(-NH_3^+)$ avec la bande de la vibration d'extension antisymétrique du groupement $-COO^-$, ayant les maximums correspondants à 1 610 cm^{-1} et respectivement à 1 582 cm^{-1}. Par deutérisation le spectre devient plus simple dans ce domaine, en se conservant la bande.de la vibration d'extension antisymétrique du groupement $-COO^-$ à 1 590 cm^{-1}, tandis que la bande correspondante $\delta_{as}e(-ND_3^+)$ se situe à 1 177 cm^{-1}. Le reste des bandes liées aux différents mouvements du groupement $-NH_3^+$

Tableau 1

L-lanthionine normale $S(CH_2CH(NH_3^+)COO^-)_2$			*L*-lanthionine deutérisée $S(CH_2CH(ND_3^+)COO^-)_2$		
2 975 é.			2 980 m.		
2 922 t.i.			2 945 f.	$\nu_{as}(CH_2)$	
2 840 f.	$\nu(NH_3^+)$	(ν_1) $\nu_{as}(CH_2)$	2 880 f.	$\nu_s(CH_2)$	
2 700 f.		(ν_2) $\nu_s(CH_2)$	2 788 m.	ν(CH)	
2 627 f.		(ν_3) ν(CH)			
2 593 é.	NH ... O	(ν_4)			
2 350 t.f.			2 380 é.		
2 320 t.f.			2 345 é.		(ν_1')
			2 248 i.	$\nu(ND_3^+)$	(ν_2')
			2 210 é.		(ν_3')
			2 183 é.		(ν_4')
			2 150 f.	NH ... O	(ν_5)
2 072 m.	NH ... O	(ν_5)			
			1 987 f.		(ν_5')
1 610 t.i.	$\delta_{as}e(NH_3^+)$	(ν_6)			
1 582 t.i.	$\nu_{as}(COO^-)$		1 590 t.i.	$\nu_{as}(COO^-)$	
1 525 é.					
1 507 t.i.	$\delta_s(NH_3^+)$	(ν_7)			
1 403 é.					
1 388 t.i.	$\nu_s(COO^-)$		1 397 i.	$\nu_s(COO^-)$	
1 348 i.	$\delta(CH_2)$		1 343 i.	$\delta(CH_2)$	
1 307 m.	δ(CH)		1 298 i.	δ(CH)	
			1 265 t.f.		
1 258 m.	$\tau(CH_2)$		1 255 t.f.	$\tau(CH_2)$	
1 242 f.					
1 222 m.	$\omega(CH_2)$		1 222 t.f.	$\omega(CH_2)$	
			1 210 f.		
			1 177 i.	$\delta_{as}(ND_3^+)$	(ν_6')
			1 161 i.		
1 136 i.	$\tau(NH_3^+)$	(ν_8)			
1 116 é.					
1 069 m.	$\rho(CH_2)$		1 063 t.f.	$\rho(CH_2)$	
			1 035 t.f.	$\delta_1(ND_3^+)$	(ν_7')
			1 007 t.f.		
			983 t.f.		
			973 t.f.		
952 i.			948 é.		
			937 t.f.		
	ν_1(CCN) + ν(CC)		914 t.f.		
903 i.			903 t.f.	ν_1(CCN)	
898 é.			880 t.f.	ν(CC)	
			868 é.		
			857 m.		
825 t.f.			835 m.		
			825 é.		
807 i.	$\rho(NH_3^+)$	(ν_9)			
			810 t.f.		
			792 m.	$\tau(ND_3^+)$	(ν_8')
			707 é.		
712 i.	$\tau(COO^-)$		699 m.	$\tau(COO^-)$	
684 t.i.	$\omega(COO^-)$		685 t.f.	$\omega(COO^-)$	
660 m.	? ν(C—S)		664 é.	? ν(C—S)	
			649 i.		
541 t.i.	$\rho(COO^-)$		543 é.	$\rho(COO^-)$	
			535 é.		
413 t.i.	déformation squelette		519 i.	$\rho(ND_3^+)$	(ν_9')
			414 é.		
			405 m.	déformation squelette	

Abréviations

é=épaule f=fort t=très
i=intense m=moyen


TRANSMITTANCE (%)
4000
3500
3000
2500
2000
1500
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1200
1100
1000
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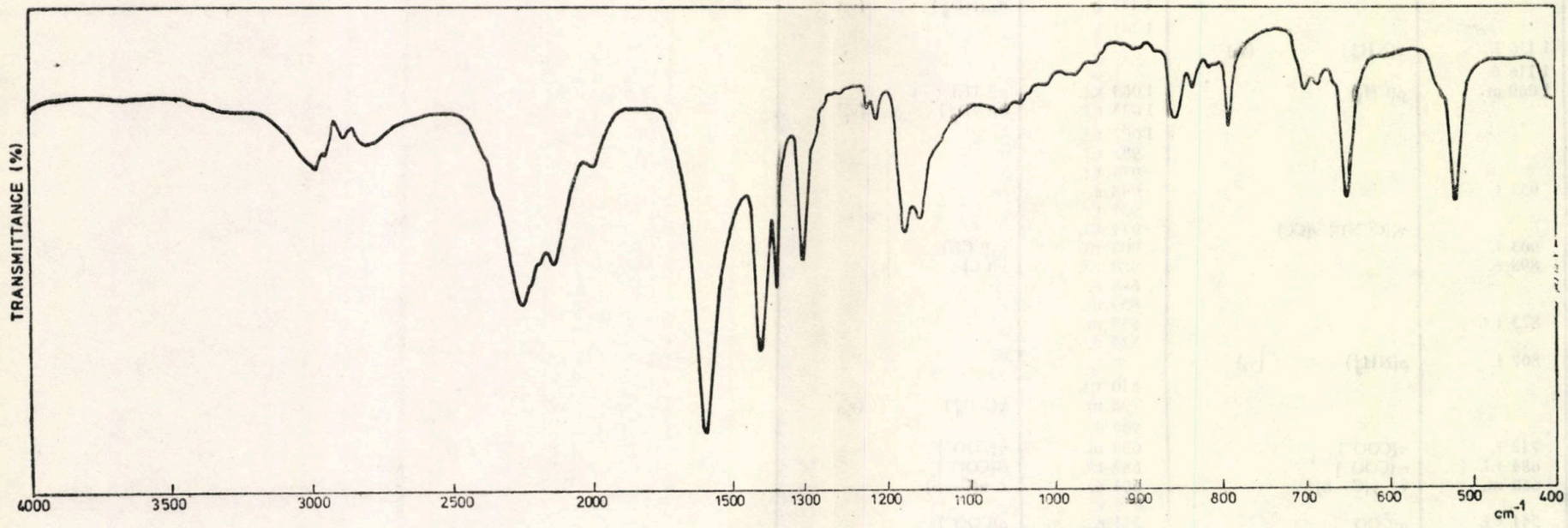
600
500
400
cm-1

Fig. 1


TRANSMITTANCE (%)
4000
3500
3000
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1100
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900
800
700
600
500
400
cm-1

Fig. 2

sont facilement à attribuer si l'on tient compte des rapports de déplacement à la deutérisation dans le cas des autres acides aminiques [1], [6], [8]. Ainsi, dans le spectre de la substance normale, les bandes se trouvant à 1 507 cm^{-1}, 1 136 cm^{-1} et 807 cm^{-1} représentent les vibrations $\delta_s(-NH_3^+)$, $\tau(-NH_3^+)$ et $\rho(-NH_3^+)$, puisque se retrouvent dans le spectre de la substance deutérisée, pour le groupement $-ND_3^+$, aux positions suivantes : 1 035 cm^{-1}, 792 cm^{-1} et 519 cm^{-1}, en bonne concordance avec les travaux précédents [1], [6], [8].

On peut, toutefois, attribuer facilement les bandes qui apparaissent encore grâce aux vibrations du groupement carboxilique. Ainsi, la vibration d'extension symétrique $\nu_s(-COO^-)$ est représentée par la bande à 1 388 cm^{-1} et correspondante à 1 397 cm^{-1} dans le spectre de la substance deutérisée. Sont encore présentes les bandes $\tau(-COO^-)$, $\omega(-COO^-)$ et $\rho(-COO^-)$ aux positions 712, 684 et 541 cm^{-1} dans le spectre de la substance normale et respectivement à 699, 685 et 543 cm^{-1} dans le spectre de la substance deutérisée. Ces attributions ont été établies compte tenu de celles précédentes [1] ... [10], [13] ... [17].

Selon les caractéristiques [7] ... [10] et compte tenu des travaux antérieurs il est tentant à admettre la probabilité que la bande se trouvant à 660 cm^{-1} dans le spectre de la substance normale, qui se maintient comme une épaule dans le spectre du composé deutérisé à 664 cm^{-1}, appartient à la vibration d'extension $\nu(C-S)$. Si la substance se présente dans une forme géométrique de sorte que les deux restes de l'alanine se trouvent d'un côté et de l'autre côté d'un plan qui passerait par le squelette C—S—C, d'une telle manière que l'énergie potentielle de la molécule soit minimum pour présenter un maximum de stabilité, alors l'atome de soufre se trouverait dans le centre de symétrie de la molécule et la vibration serait inactive en IR. À l'appui de cette hypothèse paraissent venir les fendages des bandes de vibration du groupement $-NH_3^+$, qui indiqueriont des positions spatiales différentes de ce groupement. Cette supposition doit être confirmée à l'aide des études de spectroscopie Raman et de diffraction des radiations X.

Les vibrations des groupements $=CH-$ et $-CH_2-$ donnent des bandes normales qui ne réclament pas une discussion plus ample. Apparaissent encore des vibrations de squelette et des harmoniques de petite intensité, ce qui enrichit le spectre, pendant que les vibrations dégénerées reduissent le nombre des vibrations normales.

On considère que par l'attribution des bandes aux mouvements des atomes existant dans les groupements réactifs de la molécule de lanthionine on contribue à la clarification de la structure de cet acide thioaminique et également de son comportement dans les processus chimiques.

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STUDIUL SPECTRULUI INFRAROȘU AL 3,3′-TIODIALANINEI (*L*-LANTIONINA)

(Rezumat)

Se prezintă un studiu detaliat al spectrului în infraroșu al *L*-lantioninei. Pentru obținerea spectrului s-a folosit substanța în stare solidă pastilată în bromură de potasiu, dar și în suspensie în nujol. Spectrul s-a înregistrat pentru substanța în stare normală precum și pentru compusul deuterizat la atomul de azot. Se analizează rezultatele obținute și se atribuie benzile de absorbție pentru grupele componente ale substanței cercetate. În literatură nu s-au găsit referiri cu privire la spectrul în infraroșu pentru lantionină.

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CHIMIE ȘI INGINERIE CHIMICĂ

D.C. 542.958.3 ; 541.454

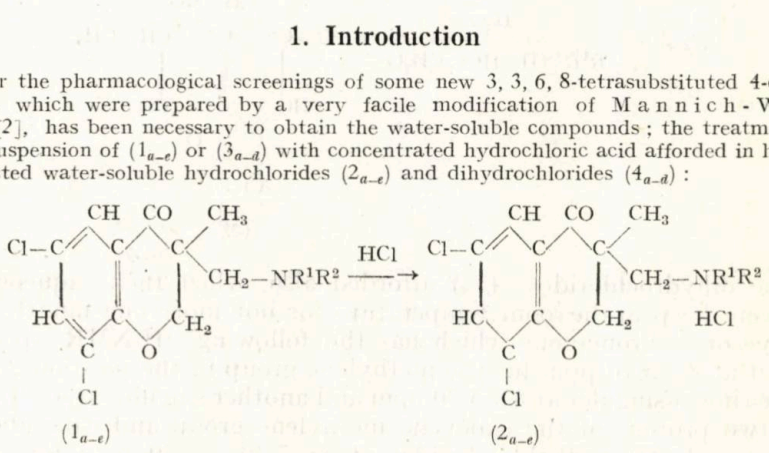
SYNTHESIS OF SUBSTITUTED 4-CHROMANONES BY „DEAMINATION" OF THE CORRESPONDING MONO- AND BIS-MANNICH BASES

BY

AL. CAȘCAVAL, HANS-JOACHIM CANTOW and GERHARD WEGNER

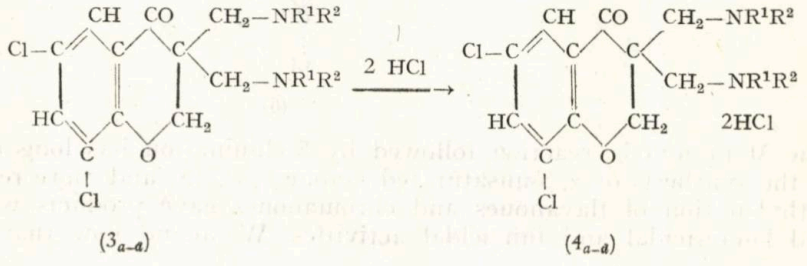
1. Introduction

For the pharmacological screenings of some new 3, 3, 6, 8-tetrasubstituted 4-chromanones [1], which were prepared by a very facile modification of Mannich-Werner reaction [2], has been necessary to obtain the water-soluble compounds ; the treatment of an acetone suspension of (1_{a-e}) or (3_{a-d}) with concentrated hydrochloric acid afforded in high yield the expected water-soluble hydrochlorides (2_{a-e}) and dihydrochlorides (4_{a-d}) :



(1_{a-e}) (2_{a-e})

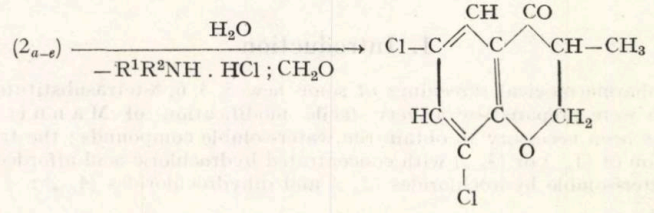
1,2,3,4	R^1	R^2
a	CH_3	CH_3
b	$-(CH_2)_4-$	
c	$-(CH_2)_5-$	
d	$-CH_2-CH_2-O-CH_2-CH_2-$	
e	C_2H_5	C_2H_5



(3_{a-d}) (4_{a-d})

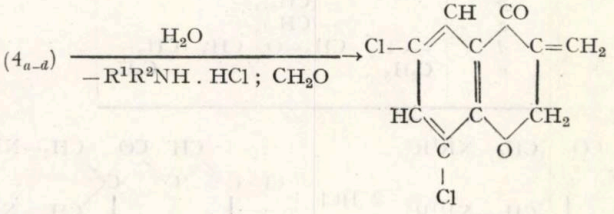
2. Theoretical

It is interesting to note that an aqueous solution of (2_e) afforded over a period of six months, by keeping at the room temperature, a crystalline white compound which has the following ^{1}H-NMR spectrum : a doublet at $\delta = 1.15 \ldots 1.30$ ppm for methyl aliphatic group, a multiplet at $\delta = 2.70 \ldots 3.20$ ppm for one proton, a multiplet at $\delta = 4.00 \ldots 4.70$ ppm for one methylene group and a double doublet at $\delta = 7.40 \ldots 7.70$ ppm for the two *meta*-coupled aromatic protons. Its IR spectrum in KBr showns a band at 1 690 cm^{-1} due to the carbonyl (ketonic) group. These findings also microanalytical analysis lead us to give the structure (5) for the product so obtained. All mono-M a n n i c h bases as hydrochlorides (2_{a-d}) afforded in a similar *„deamination"* a reversible M a n n i c h reaction [3] the same product (5) characterised as 6,8-dichloro-3-methyl-4-chromanone :



(5)

The dihydrochlorides (4_{a-d}) afforded also, when their aqueous solutions were keep at the room temperature for not more one month, a new derivative of 4-chromanone which has the following ^{1}H-NMR spectrum : a singulet at $\delta = 5.10$ ppm for the methylene group in the position *2* for the γ-pyrone ring, a singulet at $\delta = 5.70$ ppm and another singulet at $\delta = 6.25$ ppm for the two protons of the exocyclic methylene group and (like above for the compound (5)) a double doublet at $\delta = 7.40 \ldots 7.70$ ppm for the two *meta*-coupled aromatic protons ; its IR spectrum in KBr displayed bands at 1 680 cm^{-1} (carbonyl ketonic group) and 1 620 cm^{-1} (due to the exocyclic ethylenic bond). Based on these findings the new product was identified as 6,8-dichloro-3-methylene-4-chromanone (6) :



(6)

The M a n n i c h reaction followed by β-elimination has long been used to the synthesis of α, β-unsaturated ketones [4], [5] and more recent [6], methylenation of flavanones and chromanones gave products which exhibited bactericidal and fungicidal activities. We found now that the

mild conditions employed for the isolation of the exocyclic α,β-unsaturated ketone as derivative of 4-chromanone with no by-products is an excellent method for the synthesis of substituted 4-chromanones with promising biological properties. The screening of these properties for the new substituted 4-chromanones are in progress.

3. Experimental

a) *The Hydrochlorides of Mono-Mannich Bases* (2_{a-e}) *and Dihydrochlorides of Bis-Mannich Bases* (4_{a-d}). *General Procedure.*

To a suspension of the mono-Mannich base (1_{a-e}) or bis-Mannich base (3_{a-d}) (1 mmol) in acetone (25 ml) is added under vigorous stirring at the room temperature concentrated hydrochloric acid (5 ml) until a clear solution is obtained (5...15 min.) After 2 hrs. the formed precipitate was filtered off and recrystallized from absolute methanol (s. Table 1).

Table 1

Substituted 4-Chromanones (2_{a-e}), (4_{a-d}), (5)) *and* (6)) *Prepared*

Product	m.p. °C	Yield*) %	IR(KBr) ν, [cm^{-1}]
(2_a)	193	62	2 900, 2 600, 1 690, 1 590, 1 210, 800
(2_b)	190...191	76	2 940, 2 500, 1 685, 1 600, 1 200, 760
(2_c)	195...196	86	2 950, 2 500, 1 690, 1 600, 1 200, 780
(2_d)	205...206	85	2 900, 2 600, 1 690, 1 600, 1 200, 800
(2_e)	186	54	2 940, 2 500, 1 685, 1 590, 1 200, 800
(4_a)	160...162	54	3 100, 2 600, 1 685, 1 600, 1 200, 780
(4_b)	173	95	3 050, 2 650, 1 690, 1 210, 790,
(4_c)	226	45	2 900, 2 600, 1 685, 1 600, 1 200, 800
(4_d)	189...190	53	3 050, 2 550, 1 690, 1 600, 1 200, 780
(5)	114...115	45 (from (2_a) 58 (from (2_b) 50 (from (2_c) 52 (from (2_d) 58 (from (2_e)	3 050(CH aliphatic), 1 690(CO-pyrone), 1 600(aromatic ring), 1 200(C—O—C).
(6)	105...107	60 (from (4_a) 64 (from (4_b) 51 (from (4_c) 57 (from (4_d)	3 050(CH aliphatic), 1 680(CO-pyrone), 1 620(ethylenic bond), 1 210(C—O—C).

*) All new compounds (2), (4)...(6) gave satisfactory microanalysis (C±0.25; H±0.20; N ± 0.20; Cl ± 0.35%). ^{1}H-NMR spectra were recorded in $CDCl_3$ at 20°C with TMS as intern standard.

b) *„Deamination" of the Hydrochloride* (2_e)...(5)

A solution of 6,8-dichloro-3-diethylaminomethyl-3-methyl-4-chromanone (2_e) (1 mmol) in water (250 ml) was allowed to stand at the room temperature for six months. The white crystalline product is extracted with methylene chloride (2 × 25 ml), washed with water (2 × 50 ml), dried over anhydrous sodium sulphate; the solvent is removed to give pure product (5). The same product was obtained by using all hydrochlorides 2_{a-d} (s. Table 1).

c) *„Deamination" of the Dihydrochlorides* (4_{a-d})...(6).

Working out as above, after one month (1 mmol of each product 4 in 250 ml water) was obtained the sole crystalline product (6) (s. Table 1).

* * *

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SINTEZA 4-CROMANONELOR SUBSTITUITE PRIN „DEZAMINAREA" MONO- ŞI BIS-BAZELOR MANNICH CORESPUNZĂTOARE

(Rezumat)

Necesitatea preparării unor cromanone-4 fiziologic active care să poată fi administrate sub formă de soluţie apoasă a condus la o interesantă reacţie de obţinere a unor derivaţi substituiţi atît în homociclu cît şi în heterociclu; reacţia de „dezaminare" a clorhidraţilor monobazelor Mannich (2_{a-e}) conduce la unul şi acelaşi compus şi anume 6,8-diclor-3-metilcromanona-4 (5); diclorhidraţii bis-bazelor Mannich (4_{a-d}) conduc de asemenea, printr-o reacţie de scindare a aminalilor corespunzători, la un compus unic în toate cele patru cazuri şi anume la 6,8-diclor-3-metilen-cromanona-4 (6). În lucrare sînt redate procedeele generale de sinteză iar compuşii preparaţi sînt caracterizaţi din punct de vedere analitic şi spectral.

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EXTRUSION CHARACTERISTICS OF SOME POLY(VINYL CHLORIDE) BLENDS

BY

M. RUSU and MARIA LUNGU

1. Introduction

Utilisation of the compatibility agents in order to improve processing and end-use properties of the heterogeneous polymer blends (polymer blends, formulations containing filling materials, etc.) is a subject intensively studied in the last years [1] ... [3]. Consequently, taking into account the importance of the necessity of using filling materials in the processing of PVC blends [4] ... [7] and the possibility of the improving their properties by the addition of the macromolecular impact modifiers, this paper presents the data concerning the influence of the chlorinated polyethylene (CPE) charges on the extrusion formation characteristics of the unplastified PVC blends, with and without addition of the clay as filling material.

2. Experimental

To study the influence of CPE as an impact modifier on the processability of unplasticized PVC blends, with and without clay, the following materials were used : a) PVC (type 67 SD) produced by Petrochemical Plant, Borzești, Romania ; b) tribasic lead sulphate ; c) lead soap ; d) calcium stearate ; e) stearine ; f) chlorinated polyethylene (type CPE 3 614 A) produced by Dow Chemical, USA (Table 1) ; g) fine grade clay, produced by Mining Exploitation Aghireș, Romania (Table 2).

The studied blends have been prepared using the following receipt (parts by weight) : PVC 100, lead basic trisulphate 2, lead soap 2, calcium stearate 0.3, stearine 0.15 to wich clay (0 and 10 parts) and CPE (parts between 0 and 10) have been added. The mixing of the components has been accomplished in a TRUSIOMA mixer (GDR) at 3 000 rpm.

The mixtures thus obtained, as dry blends, have been used for determining the extrusion characteristics of the materials. For this purpose a Göttfert (FRG) extrusiometer with the screw diameter $D = 20$ mm, compression ratio of 3 : 1 and relative length $L/D = 20$ has been used. The apparatus was provided with temperature and pressure transducers for measuring the axial pushing (counterpressure) and the screw torque. By means of this apparatus the pressure and temperature of mixture melts in the zones $11D$, $16D$ and $20D$, the counterpressure, the torque and the

Table 1

The Characteristics of the Chlorinated Polyethylene CPE 3 614[1])

Characteristics	Values
Chlorine content, [%]	36.0
Residual crystallinity, [%]	2.0
Bulk density, [Kg/m^3]	420
Specific gravity, [Kg/m^3]	1 160
Volatiles, [%]	0.2
Melt viscosity, [Pa.s]	21.5×10^{-4}
Typical screen analysis retained on 20 mesh, [%]	5.0
100% Moduls, [MN/m^2]	2.0
Tensile strenght, [MN/m^2]	8.4
Elongation at break, [%]	700
Hardness, Shore A (10 s)	53
Izod impact, notched, [J/m]	980
Low temperature brittleness, [°C]	−68

[1]) Obtained by the chlorination of low pressure polyethylene.

Table 2

Characteristics of the Clay

Characteristics	Values
Appearance	grey powder
Moisture content	max. 1.0%
Residue of 0.063 screen	max. 0.05%
Aluminium trioxide	min. 34%
Ferric oxide	max. 1.3%
Silica	max. 63%
Losses by calcination	max. 1.0%

weight flow rate (by collecting and weighing the extruded material) have been determined.

To find the extrusion characteristics, a circular die (d=2 mm, l= =30 mm) has been used. The temperature of the termal zones of the extrusiometer have been fixed as follows: zone *I* — 182°C, zone *II* — 196°C, zone *III* — 196°C. The measurements have been carried out in a range of screw speeds comprised between 20 and 80 rpm.

The viscosity of the mixture melts was calculated according to a method previously described [8].

3. Results and Discussion

Based on the readings from the extrusiometer and on the data resulting from calculations, curves were plotted in order to reveal the variation

of the extrusion characteristics against the CPE content, for the blends without the filling material and those with 10 parts clay, at screw speed of 20 and 80 rpm.

Since in the zone $11D$ the blends are not entirely plastified and homogenized, which is evidenced by the fact that the pressure in this zone largely varies, the settling of a certain manner of pressure variation is a very difficult task. However, it could be estimated that for the blends without clay the pressure in the zone $11D$ will exhibit a minimum value for a content of 5.5 parts of impact modifier in the compounds. In case of mixtures containing clay a minimum also occurs whose position is shifted to a content of 7.0 parts. For clay containing blends the pressure in the zone $11D$ are higher than those corresponding to the blends with no filling material.

By the analysis of the manner in which varies the other extrusion characteristics (except the flow rate) versus the CPE content from the blends and screw speed, one can found out the followings conclusions :

For the blends with no filling material, at low screw speeds, the investigated extrusion characteristics (except for the weight flow rate) exhibit minimum and maximum values for CPE contents of 2.5 and 5.5 parts respectively (Fig. 1 *a*). This manner of variation is characteristic to a wide series of polymers and is due to the interactions occuring between the system components during mixing [9]. With increasing screw rate the maximum and minimum of the curves considerably attenuate, which can be accounted for by the increase of the shear stresses in the system (Fig. 1 *b*).

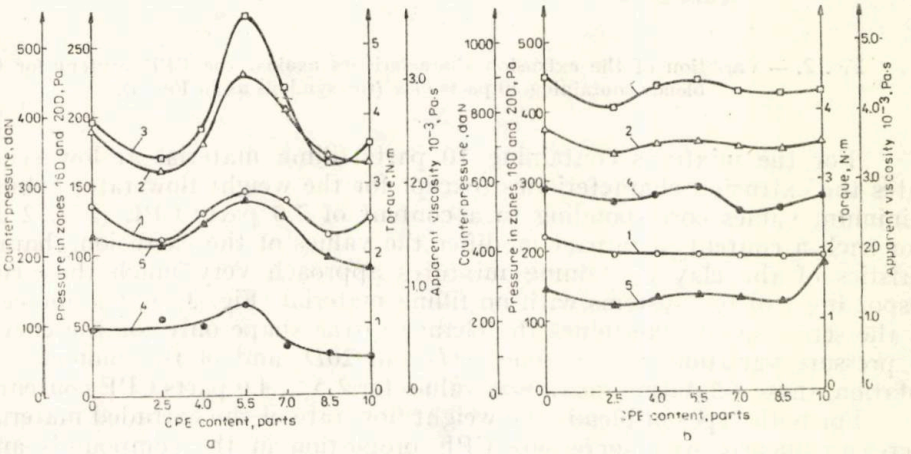

Fig. 1. — Variation of the extrusion characteristics against the CPE content for the blends without clay : *1* — pressure at $16D$; *2* — pressure at $20D$; *3* — counterpressure ; *4* — torque ; *5* — apparent viscosity ; *a* — 20 rpm ; *b* — 80 rpm.

The introduction of 10 parts clay into the blends determines leads too considerable modification of the aspect of the curves depicting the variation of extrusion characteristics as a function of CPE content as compared to the blends with no filling material (Fig. 2). This fact is normal, since it is known that the presence of filling material in the polymer blends

determines the increase of their viscosity, and therefore of the pressure in the barrel, of the counterpressure in the bearing, and of the torque [10]. This means that the clay containing blends will be hardly worked and with higher power consumption than those with no filling material. The different shapes of the curves corresponding to the clay containing blends can be also attributed to the modification of the ratio between the internal and external lubrication actions of the components of the system [11].

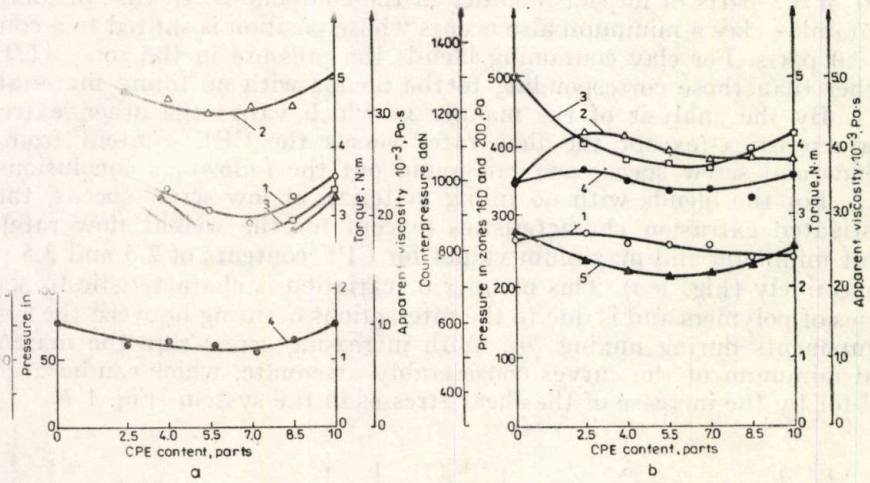

Fig. 2. — Variation of the extrusion characteristics against the CPE content for the blends containing 10 parts clay (the symbols as in Fig. 1).

For the mixtures containing 10 parts filling material at low screw rates the extrusion characteristics (except for the weight flow rate) exhibit minimum values corresponding to a content of 7.0 parts CPE (Fig. 2 *a*). For such a content of impact modifier the values of the extrusion characteristics of the clay containing mixtures approach very much those corresponding to the systems with no filling material (Fig. 2 *b*). The increase of the screw speed determines the change of the shape only for the curves of pressure variation in the zone $11D$ and $20D$ and of the moments of rotation, these exhibiting maximum values for 2.5 ... 4.0 parts CPE contents.

For both types of blends the weight flow rate of the extruded material increases linearly with increasing CPE proportion in the compounds and with screw speed. The increase as a function of CPE content is less significant in case of mixtures with no filling material and more accentuated for the compounds with clay.

4. Conclusions

The curves of variation of the main extrusion characteristics (except for the weight flow rate of extruded material) as a function of CPE content in the unplasticized PVC compounds exhibit shapes characteristic to polymer

blends. The introduction of 10 parts clay in these blends determines the modification of the shapes of the curve, the latter exhibiting a minimum at a content of 7.0 parts CPE in the blends. For such a content of impact modifier, the values of extrusion characteristics approach very much those of the compounds with no filling material.

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CARACTERISTICILE DE EXTRUDERE ALE UNOR AMESTECURI PE BAZĂ DE POLICLORURĂ DE VINIL

(Rezumat)

S-a studiat influența adaosurilor de polietilenă clorurată (CPE 3614 A) și a vitezei de rotație a melcului asupra caracteristicilor extruziometrice ale amestecurilor neplastifiate de PVC, cu și fără adaos de caolin ca material de umplutură.

Pentru amestecurile fără material de umplutură, curbele de variație a principalelor caracteristici extruziometrice (cu excepția debitului de material extrudat) au forme caracteristice amestecurilor de polimeri. Introducerea în aceste compounduri a 10 părți caolin determină modificarea formei curbelor, ele prezentînd un minim la 7,0 părți CPE 3614 A în sistem. Pentru un asemenea conținut de CPE (modificator de șoc), valorile caracteristicilor extruziometrice ale amestecurilor conținînd 10 părți caolin se apropie cel mai mult de cele ale compoundurilor fără material de umplutură.

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CARACTERIZATION OF POLY(ETHYLENE TEREPHTHALATE)

VI. $[\eta]-M$ RELATIONSHIP AND UNPERTURBED DIMENSIONS OF POLY(ETHYLENE TEREPHTHALATE) MODIFIED WITH DIMETHYL-ISOPHTHALATE*)

BY

C. V. UGLEA, ADRIANA MIHĂESCU and EMIL MATEI

1. Introduction

Materials obtained by the modification of poly(ethylene terephathalate) (PET) with dimethylisophthalate (DMI) are characterized by specific properties which depend on DMI amount introduced in the main chain of PET. In the industrial practice, PET modified with DMI is characterized in solution by the same relationships as for normal PET and the presence of DMI in the main chain of PET will be not taken into account when the results will be disscussed.

In this paper $[\eta]-M$ relationships specific for PET modified with DMI and the variation of their unperturbed dimensions with the amounts of DMI introduced in PET [1], [2] are determined.

2. Experimental

2.1. Reagents and Products

a) PET, industrial grade as wet chips.

b) Dimethylterephthalate (DMT), DMI and ethylene glycol (EG), industrial grade of purity suitable to fibre processing.

c) PET 7.5 and PET 25 are copolyesters obtained in the laboratory as result of DMT, DMI and EG copolycondensation [3]. The figures show DMI amount (calculated as % vs. DMT weight) used in the ester interchange step of copolyester synthesis.

3. Methods

a) *Fractionation by Coacervate Extraction.* Polyesters PET, copolyesters PET 7.5 and PET 25 were fractionated by coacervate extraction in the conditions given in a previous work [4]. In Table 1 the characteristics of the fractions resulted are given.

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*) Communication presented at the 2nd National Congres of Chemistry, Bucharest, September, 1981; the previous paper in this series is published in [17].

Table 1

The Characteristics of Fractions Separated by Coacervate Extractions

No	PET			PET 7.5				PET 25			
	$[\eta]$ dl/g	M_n	COOH eq/g. 10^6	$[\eta]$ dl/g	M_n	COOH eq/g. 10^6	DMI %	$[\eta]$ dl/g	M_n	COOH eq/g. 10^6	DMI %
1	0.22	4 700	20.0	0.11	2 200	31.0	3.8	0.20	4 500	25.0	17.3
2	0.44	11 300	27.0	0.28	7 400	31.9	5.0	0.42	13 500	25.2	16.2
3	0.48	12 600	19.0	0.47	13 300	22.7	4.4	0.45	15 100	23.3	21.0
4	0.51	13 500	34.0	0.51	14 900	32.7	4.9	0.51	16 900	23.8	20.0
5	0.52	13 600	25.0	0.56	16 700	22.6	5.2	0.52	18 000	23.2	21.0
6	0.55	14 700	30.0	0.58	17 400	23.5	9.3	0.56	20 000	21.9	25.0
7	0.64	17 800	29.8	0.64	19 700	21.4	8.9	0.59	21 000	30.0	29.2
8	0.64	18 400	29.9	0.80	27 500	28.7	8.2	0.61	21 800	33.9	29.0
9	0.74	21 800	28.7	0.87	29 500	31.3	9.6	0.63	22 400	34.0	35.0
10	0.79	23 700	29.1	—	—	—	—	0.72	30 000	35.2	33.3
11	0.80	25 000	27.0	—	—	—	—	—	—	—	—
IS*)	0.64	18 000	28.0	0.50	17 200	25.1	6.94	0.54	19 000	32.5	24.2

*) Initial samples.

b) *Determination of Molecular Weight.* Number average molecular weight ($\overline{M}_n$) of the fractions and unfractionated samples was determined by end group titration. The method described by Conix [5] was used.

c) *Determination of Unperturbed Dimensions.* Stockmayer and Fixman [6] proposed the relationship:

$$\frac{[\eta]}{M^{1/2}} = K_0 + 0.51BM^{1/2}, \tag{1}$$

to determine the unperturbed dimensions of polymer chains, where: M represents molecular weight; $K_0 = \Phi_0(\overline{r}_0^2/M)^{3/2}$; $\overline{r}_0^2$ — mean square end-to-end distance of the chain in theta conditions; $\Phi = 2.8 \times 10^{23}$.

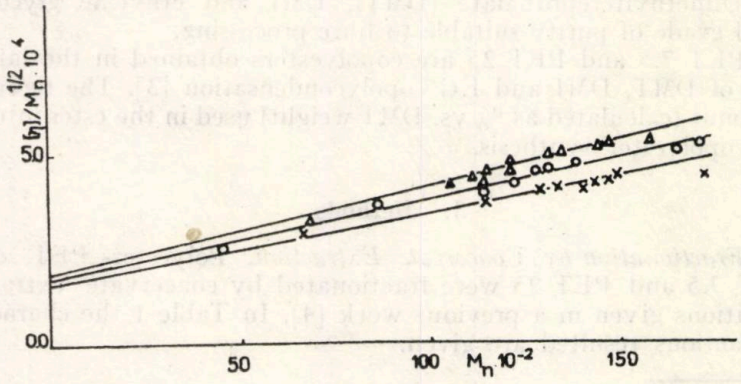

Fig. 1. — The determination of unperturbed dimensions; Δ—PET; o—PET 7.5; x—PET 25.

When the ratio $[\eta]/M^{1/2}$ is plotted vs. $M^{1/2}$ (Fig. 1) a stright line is obtained and its slope and intersection with ordinate are $0.51B$ and K_θ, respectively. K_θ obtained as above may be used to determine $\overline{r_0^2}$. Chain flexibility may be also expressed by the ratio $\overline{r_0^2}/M^{1/2}$, procedure which was used in the present work. The values obtained are given in Table 2.

Table 2

The Constants from $[\eta]=KM^a$ Relation and Unperturbed Dimensions of the Analysed Samples

Sample	$K.10^{-4}$ dl/g	a	K_θ ml/g		$(\overline{r_0^2}/M)^{1/2}\times 10^{11}$ cm	
			SF*)	A**)	SF*)	A**)
PET	2.52	0.80	0.185	0.190	871	895
PET 7.5	2.66	0.79	0.174	0.190	854	895
PET 25	5.89	0.67	0.160	0.190	829	895

*) Determined by the method of Stockmayer and Fixman [6].
**) Determined by the method of Aharoni [8].

d) *Determination of Constants from the Relationship* $[\eta]=KM^a(MH)$. When log $[\eta]$ was plotted vs. log M_n, the constants K and a were determined. The data from Table 1 were used and the results are given in Table 2.

4. Results

a) *Influence of DMI Content on Constants from MH Relationship.* According to Flory theory [7], the variation of a from MH relationship is within a range from 0.5 and 0.8. This rule is applied to flexible polymers with the condition of solvent impermeability through the macromolecular coil. The lower limit of variation range corresponds to a strong coiled configuration specific to theta conditions, while the upper limit is a characteristic of the extending configuration specific to good solvent—polymer systems. When the limit of 0.8 is exceeded, this means that the solvent was permeable through the macromolecular coil as result of the fact that macromolecular solute is as rodlike chains.

The constant K from MH equation was considered unsignificant regarding the configuration of the chain in the solution. Recently [8], the following empirical relationship was establihed :

$$\log K=C-Ba, \tag{2}$$

where K and a are constants from MH relationship and B and C are constants.

The dependence between K and a is proved by relation (2). As result the change of a will determine the modification of K.

It is well known that K and a constants from MH relationship are influenced by chemical unhomogeneity of the polymer [9]. Isophthalic structures in PET main chain have a sistematic influence on a and K from MH relationship, as it can be seen from the data given in Table 2. This

dependence may be explained by means of the data from Table 1. When the results of the fractionation are analysed it may be seen that the separation of PET 7.5 and PET 25 samples takes place according both molecular mass and chemical composition of the species. Isophtalic structures are accumulated in the fractions of high molecular mass. From the same data it may be noticed that to similar molecular masses correspond different intrinsic viscosities. This remark gave us the possibility to suppose that an increase of DMI amount in PET will modify the configuration in solution of the chain so that a more coiled configuration will be adopted. This statement is also confirmed by the unperturbed dimensions of the analysed samples.

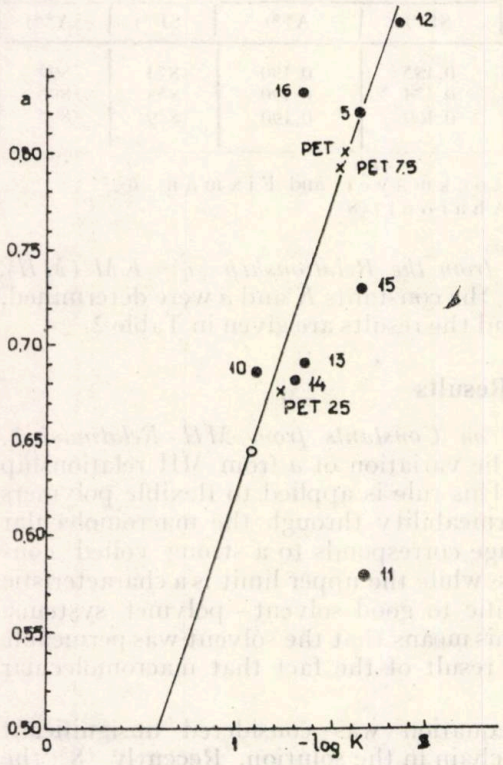

Fig. 2. — The dependence between K and a from MH relation; x—our data; o—poli(ethylene isophthalate) [1]; ●—literature data; the figure show number of reference.

Consequently it may be concluded that *a exponent will be diminished and K constant will be increased as result of the modification of PET with DMI.*

b) *Influence of DMI Content on Unperturbed Dimensions of PET Modified with DMI.* The use of SF method gave the possibility to obtain K_θ and the ratio $\bar{r}_0^2/M^{1/2}$ given in Table 2. From these data it can be noticed that when isophthalic structures are introduced in the main chain of PET a decrease of the characteristics of chain configuration in solution will result. In conclusion the data obtained prove that, compared with PET, more coiled configuration is shown by PET copolyesters with DMI.

Relationship (2), established by A h a r o n i [8], may be also used to determine the unperturbed dimensions of polymers. In the theta conditions ($a = 0.5$) relationship (2) becames:

$$\log K = C - \frac{B}{2}. \qquad (3)$$

When $-\log K$ is plotted versus a it is obtained a stright line which extrapolated at $a=0.5$ allows to obtain K. When this method is applied a single value for K_θ and for $\bar{r}_0^2/M^{1/2}$ is obtained and as result we consider A h a r o n i's method [8] as an alternative valuable only for chemical homogeneous polymers (Fig. 2 and Table 2).

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CARACTERIZAREA POLI(ETILENTEREFTALATULUI)

VI. Relaţia $[\eta] - M$ şi dimensiunile neperturbate ale poli(etilentereftalatului) modificat cu dimetil-izoftalat

(Rezumat)

Se prezintă rezultatele obţinute la caracterizarea în soluţie a poli(etilentereftalatului) modificat cu dimetiltereftalat (DMI). Corelarea valorilor maselor moleculare medii numerice cu valorile corespunzătoare ale viscozităţilor intrinseci ale fracţiunilor obţinute prin extracţie din coacervat, arată că exponentul a şi constanta K din relaţia $[\eta]=KM^a$ depind de conţinutul în DMI din poli(etilentereftalat).

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NEW SOLUTIONS FOR MODERNIZING THE EXISTENT TECHNOLOGIES IN SYNTHETIC FIBER WORKS, JASSY

BY

CORNELIU COSTICĂ CIOCAN and CARMEN TEODOSIU

1. Introduction

Generally speaking, the economic efficiency reflects the ratio between the effort made and the results, considering as efficient that activity in which the results provide both the social nood satisfaction, the efforts compensation and the obtaining of the net income. In order to increase the economic efficience it must be applied measures such as [1] : use of the producing capacities with an increased ratio, introduction and generalization of modern technological processes and asimilation of new products, the increase of productivity, the decrease of production costs, the improvement of the quality and the working conditions and the increase of rentability.

In the chemical-engineering field, we can consider that improving of the equipment and of technological processes are the two pylons which are staying at the base of the inovation with remarcable efects concerning the efficience. According to B r a u e r [2] „...standing on only one of these pylons, the innovation will be substantially embarassed".

Concerning the polymers and the synthetic fibers installations, which are based on oil, it is important to verify the technological process and the installation's design, analyzing at the same time the finit product requires and of the exploitation technology [3].

Working for competitivity, our specialists have had succeses concerning modernizing technologies and equipment, with major economical and qualitative implications. Among the performances we can mention the following :

a) *Regarding the technology's improvement*: continuous polycondensation, fibers with increased dye affinity, high speed spinning, simultaneous draw texturing, mass colouration's fibers, draw and texturing interlaced yarns.

b) *Regarding the equipment's development* : polymer grains dryer, equipment for the filtration and spinning the polymer's melting, equipment for interlacing.

2. New Proposed Technologies. Discussion

The two directions of improvement will be discussed concerning the technological advantages with implications on economics and qualitaty.

2.1. TECHNOLOGY'S IMPROVEMENT

a) *Continuous Polycondensation*. Polyethylene terephtalate is a polymer from polyesters class obtained from dymethylterephtalate and monoethylene glycol in a discontinuous process, in two steps: transesterification and polycondensation. As in the other branches of the chemical industry, the discontinuous processes, non profitable, are replaced by continuous ones in only one direction, in which the supply of starting materials and evacuation of reaction products are made continuously. The advantages of this technology are [4] :

a) Economy of starting material, because of the reduced losses :

dymethylterephtalate (DMT)	4 to
monoethylene glycol (MEG)	20 to,

reported to 1 000 to. polymer.

b) Reduced consumption of energy since the continuous process needs a constant energetical flux in order to ensure the optimal performance of the installation with the best mecanic and termic efficience :

— electric energy 15 MWh,
— pit gas 17 000 Nm^3,
— steam 30 Gcal,
— industrial water 1 900 m^3,

reported to 1 000 tone polymer.

c) The application of the continuous process at the spinning of the cable for fibers, which leads to the following advantages (connected with the reduction of the intermediate phases): cooling of grains, the intermediate storage of the grains, the grain's drying and the spinning. All these conduct to important economics of starting materials, energy, labour, initial costs of fiber, about one milion lei / 1 000 to fiber.

b) *Polyesters Fybers with Increased Dyeing Affinity.* The polyester fiber'dyeing with dispersion dyers is far from being resolved not only in our country but on the world scale, too. That is why any effort in this direction is regarded with interest. In this field we can mention the obtaining of the copolyesteric fibers with polyglycol, which can be dyed with dispersion dyers. The advantages of this technology, are the following [5] : a) the dyeing can be made directly in the spinning process or in autoclave at the boiling temperature and normal pressure ; b) copolyesteric fibers can be dyed together with natural fibers at the employer ; c) the reduction of the dyers and energy consumption.

It can be realized an economy of 974 000 lei / 100 tone fiber.

c) *The High and Moderate Speed of Spinning.* The transformation of the polymer grains in yarns takes place during the spinning process which means a succesion of technological stages. Although the conventional technologies are still used, the high speed spinning process followed by the simultaneous draw-texturing process and by thermal treatment (if necessary), is usually applied.

The high speed spinning has the following advantages [6]:

1° The increased production capacities (on spinning post) :

a) with 24% for an increase of the spinning speed from 1 000 to 1 500 m/min ;
b) with 10% for an increase of the spinning speed from 1 500 to 2 000 m/min ;
c) with 6% for an increase of the spinning speed from 2 000 to 2 500 m/min ;
d) with 3% for an increase of the spinning speed from 2 500 to 3 000 m/min ;
e) with 2% for an increase of the spinning speed from 3 000 to 4 000 m/min.

It can be observed that the passing from 1 000 to 2 500 m/min result in an increase of productivity of 40%, but over 2 500 m/min, the increase of the productivity is smaller in comparison with the energetical consumption and the initial costs.

2° The obtained yarns have a greater stability than those produced by low spinning process, because of the macromolecular orientation, which gives yarn of stabile supramolecular structure. The structural stability of yarns makes possible a long period of storage and the delivery as spin ned yarns to the users.

3° The more stable winding of the spinning bobbins due to the practicing of higher tensions and greater structure stability.

4° The spinning is possible without sliding blocks, because the tensions process which makes possible certain advantages such as the renunciation at the two sliding blocks and driving motors acting them [7]. Using the spinning without sliding blocks reduces the consumption of electric energy with 250 MWh/year.

5° The application of the simultaneous draw-texturing with all the economic and qualitative advantages which makes possible smaller residual draw ratio [8], [9].

These advantages of the high speed spinning conduct to a yearly benefit of 12 millions lei.

d) *The Simultaneous Draw-Texturing.* This technology, which is based on the high speed spinning, makes possible the obtaining of new yarn asortments with superior qualitative characteristics and economic values [10]. The advantages are, as follows :

a) The draw machines are eliminated and the initial costs are reduced with 25%.
b) The resulted bobbines are heavier.
c) The energy consumption is reduced.
d) The production of textured yarn increases due to the increased operating speed.
e) Set yarns can also be obtained.

f) The dyeing affinity is higher. With all these advantages, meaning starting supply, economies of energy, labour and superior quality ,the result is a benefit of 6.5 million lei.

e) *Mass Colouration Yarns.* By applying this technology, yarns with a higher dyeing uniformity are obtained, using a polymer which was mass coloured. It results the following advantages [11] :

a) It can be used a high speed spinning.
b) It can be used the simultaneous draw texturing.
c) Set yarns can be obtained,
d) A diminution of the operational time, low energetical consumptions and labour.
e) Yarns are dyed uniformly.

By applying this technology, annual benefits of 6.552 millions lei are obtained.

f) *Interlacing.* This technology makes possible the elimination of stages of the flow sheet with certain qualitative and economical advantages. The technology is applied for obtaining the draw and texturized yarns [12], [13].

The interlacing effect is obtained when the yarn is passed through an air blast nozzle, in which the air injection is made at a certain pressure and the environmental temperature. The air blast nozzle is placed before the draw or texturizing machine. This effect makes the yarn better bunched together and so the interlaced yarns can replace successfully the twisted ones [14], [15].

The main advantages are :

a) The elimination of the operations such: the twisting, the steam-setting and the spooling with many economical advantages.
b) The quality is improved, because of the gently dealing of the yarn.
c) The modulus of elasticity is two times higher than that of the twisted yarns.

These advantages conduct to a yearly benefit of one million lei.

2.2. THE EQUIPMENT DEVELOPMENT

Application of the mentioned technologies would have not been possible without respecting the second term of the equation : equipment development technology improvement = base of the innovation.

a) *Dryer for the Poly(ethylene Terephtalate) Grains.* The high speed spinning technology implies certain demands of the starting supply such as : the uniformity of grains regarding their characteristics, without dust, humidity under 100 ppm (in order to prevent the hydrolitic destruction reactions). This last demand was realised by using a new dryer and by realisation of an adequate technology. This dryer differs from other equipments, namely, it is fitted with a precrystallization before the drying operation. The main advantages are [6] :

a) The decreasing of the grains sticking in the drying process which eliminates the interruptions in obtaining the spinning yarns. The grains consumption decrease with 5 Kg/tone of spinning yarn.
b) The drying process is more efficient, the grains humidity is under 80 ppm.
c) The recuperation of the drying heat and the use of it in the precrystallization process.

Using this kind of dryer and the proposed technology, the economies are of 0.9 millions lei.

b) *Static System of Dedusting and Burrs Removal of Polymer Grains.* During the polymer granulation due to the granulator knives, there appear grains dust, grains with burrs, which in the drying and spinning process conduct to the clogging of the equipment and non-uniform characteristics. So, when entering the hoppers of the spinning installation, sizers are placed. The motric force of the separation is provided by the pressure of the air [17].

c) *Device for the Filtration and Spinning of the Polymer Melt.* The high speed spinning implies also the advanced filtration of the polymer melt, which is possible by using the efficient filtration materials and adequate ratios [18]. Using this system of filtration and spinning, there are saved 0.25 millions lei [19].

d) *Device for the Interlacing.* For the improval of the work conditions to decrease the time for the yarns' catching and for the elimination of import such devices were perfereted [20].

3. Conclusions

The discussed examples denote that the technical progress in the polymer industry of fiber and polyesteric yarns is based on the technical innovation which is supported by the improvement of technology and development of equipment.

The equation: technology improvement + equipment development = the innovation base, implies the simultaneous respecting of the left-side terms of the equation.

Economies of starting supplies and energy can be made in the technological processes almost standardized today.

Actual and future concerns, are directed towards the equipments in order to diversify the assortments (effect yarns, yarn with high twists and low average titles, which confers to the textile products softness and the improvement of the dyeing affinity, etc.), the reduction of the starting supplies of the energy consumption and the improvement of the work conditions.

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NOI METODE DE MODERNIZARE A TEHNOLOGIILOR EXISTENTE ÎN COMBINATUL DE FIBRE SINTETICE, IAȘI

(Rezumat)

Sînt prezentate, sub aspectul eficienței și creșterii calității, unele din noile tehnologii cum ar fi : policondensarea continuă, vopsirea în masa de reacție, filarea rapidă, etirarea, texturarea simultană etc., aplicate în producerea de fibre și fire din poli(etilen tereftalat).

BULETINUL INSTITUTULUI POLITEHNIC DIN IAȘI
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CHIMIE ȘI INGINERIE CHIMICĂ

CONSTANTIN H. BUDEANU

1915—1987

La 25 octombrie 1987 a încetat din viață Constantin B u d e a n u, profesor doctor docent la facultatea de Tehnologie Chimică a Institutului politehnic din Iași.

Născut la 1 august 1915, în satul Drăgănești, jud. Bălți, a urmat cursurile școlii primare în satul natal și, apoi, cele ale liceului „I. Creangă", secția reală, din orașul Bălți, pe care le-a absolvit în anul 1936. În același an se înscrie la Facultatea de Științe a Universității „Al. I. Cuza", secția tehnologică, iar în 1938, se transferă la facultatea de Chimie industrială a Politehnicii din Iași și obține diploma de inginer în anul 1940.

Remarcat din timpul studenției, la terminarea facultății Constantin B u d e a n u devine asistentul profesorului C. V. G h e o r g h i u de la catedra de Chimie organică a Universității din Iași. În anul 1948 obține titlul de doctor în științe chimice cu mențiunea *Magna cum laudaea*.

La 24 februarie 1942 este promovat șef de lucrări, apoi la 1 decembrie 1948 devine conferențiar. De la 1 octombrie 1962 este profesor universitar titular la catedra de Chimie organică a Universității din Iași.

În anul 1969 i s-a acordat dreptul de a conduce doctorate, iar în 1971 își trece examenul de docență.

În perioada 1974—1980 a funcționat în calitate de profesor de Chimie organică la facultatea de Tehnologie chimică de la Institutul politehnic din Iași, în urma fuzionării facultăților de chimie și chimie industrială.

Profesorul Constantin B u d e a n u a desfășurat timp de peste 40 de ani o bogată activitate didactică și științifică, după pensionare (în anul 1980) depunînd o susținută activitate de cercetare, ca profesor consultant.

Începînd din anul 1949 a desfășurat, timp de aproape un deceniu, o activitate laborioasă în cadrul Institutului de chimie al Academiei, în calitate de cercetător și colaborator științific, obținînd rezultate de prestigiu.

Înzestrat cu alese calități intelectuale, însuflețit de un puternic entuziasm creator, dăruit trup și suflet școlii, Constantin B u d e a n u a reușit să fie un dascăl și un om de știință model pentru noi toți. Munca depusă de profesorul B u d e a n u la catedră și ca cercetător reprezintă efortul plin de abnegație al unei minți luminate și a unui cuget ales, în slujba unei cauze nobile.

Cursurile predate de profesorul B u d e a n u s-au remarcat prin înaltă ținută științifică, prin deosebite calități didactice, prin bogăția și logica impecabilă a faptelor expuse.

Pasiunea incandescentă pentru cercetarea științifică, care nu l-a părăsit toată viața, și-a avut rădăcinile în convingerea că are ceva de spus, că, și în acest fel, va fi mai folositor colegilor, colaboratorilor și școlii. Apropiat de cei tineri, fie că erau studenți, doctoranzi sau colaboratori, profesorul B u d e a n u reușea prin exemplul său, prin munca perseverentă, să-i antreneze într-un efort susținut și încununat de roade.

Opera ştiinţifică a profesorului Constantin B u d e a n u, concretizată în peste 120 lucrări ştiinţifice, publicaţii, brevete, reflectă preocuparea sa permanentă pentru îmbinarea cercetării fundamentale cu cercetarea aplicată. Rezultatele sale ştiinţifice s-au concentrat mai ales în domeniul sintezei şi caracterizării unor noi combinaţii organice cu proprietăţi biologic-active. Unul din domeniile abordate de profesorul B u d e a n u, inaugurat prin teza sa de doctorat, îl constituie studiul acţiunii izotiocianaţilor asupra oximelor.

Alegînd o serie de izotiocianaţi de alchil sau aril, profesorul B u d e a n u reuşeşte să pună în evidenţă reacţii originale, deosebit de interesante, ca de exemplu : izomerizarea optică a levomentonoximei sub acţiunea izotiocianatului de benzoil sau reacţia dintre izotiocianatul de naftil şi o serie de sulfamide şi acizi aromatici. În vederea obţinerii unor medicamente originale româneşti, Constantin B u d e a n u a dedicat mult timp găsirii unor substanţe cu acţiune antituberculostatică din diferite clase, cum sînt : hidrazidele, tiourei conţinînd grupări sulfamidice, azometine, esteri ai acizilor *p*-amino-benzoici etc.

Cu aceeaşi pasiune şi statornic optimism profesorul B u d e a n u a abordat domeniul deosebit de actual al medicamentelor citostatice. Împreună cu colaboratorii săi a sintetizat un mare număr de azotiperite cu activitate antitumorală potenţială, conţinînd resturi de acizi aminici, cum ar fi acidul asparagic şi glutamic.

Mereu în căutarea unor noi structuri biologic-active, Constantin B u d e a n u, integrîndu-se în tradiţia şcolii ieşene de chimie organică, a preparat o serie de derivaţi de triazol, tiadiazol, imidazoli, chinazoline, dintre care unii manifestă interesante proprietăţi fiziologice (hipotensoare ş.a.).

Cercetările profesorului B u d e a n u în domeniul obţinerii de noi polimeri, obţinerea unor complecşi cu cupru şi zinc ai unor tiosemicarbazide, prezintă un pronunţat caracter de originalitate. Analiza atentă a întregii opere ştiinţifice pe care a lăsat-o scoate la iveală alesele calităţi de om de ştiinţă ale profesorului B u d e a n u. Opera sa reflectă o imaginaţie vie, mereu în căutarea datelor noi, un entuziasm şi un optimism înflăcărat însoţite de seriozitatea şi prudenţa necesare înţelegerii juste a faptelor. Pasiunea sa pentru ştiinţă a fost permanent susţinută de cumpătarea înţeleptului, de firească luciditate a creatorului de talent. O atare activitate prodigioasă în domeniul sintezei organice i-a atras o binemeritată recunoaştere şi apreciere nu numai în ţară ci şi dincolo de graniţele ei, prin alegerea sa ca membru al societăţii franceze de terapeutică şi farmacodinamie şi ca membru titular al societăţii franceze de chimie.

Numeroasele medalii şi ordine cu care a fost distins profesorul B u d e a n u vin să confirme, încă o dată, meritele sale deosebite pentru propăşirea ştiinţei şi culturii în ţara noastră.

Munca neobosită a profesorului Constantin B u d e a n u, pusă în slujba învăţămîntului şi cercetării adevărului ştiinţific, rămîne un viu exemplu pentru toate generaţiile de chimişti ce vor urma.

Prof. dr. doc. Magda Petrovanu
Şef lucr. dr. Valeriu Şunel

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RECENZII

BOOK REVIEWS РЕЦЕНЗИИ

KOTAS T. J., *The Exergy Method of Thermal Plant Analysis*. Butterworths, London, Boston, Toronto, 1985, XIX + 296 pp.

The exergy method is a relatively new technique based on the concept of *exergy*, defined as a universal measure of the quality of different forms of energy in relation to a given environment. This is the first comprehensive book on this subject.

Chapter 1 gives a review of the fundamentals of classical thermodynamics. A particular emphasis is put on the Second Law which leads to the concept of entropy production — a subsidiary concept in the subsequent development of some basic exergy relations. Chapter 2 introduces the concepts on which the exergy method is based : the concept of exergy, physical exergy, chemical exergy, exergy concepts for closed system analysis, non-flow exergy. Chapter 3 introduces the techniques which use the basic concepts of the method in plant *analysis*. The exergy balance and the rational efficiency are defined for closed as well as for open systems. Chapter 4 studies the simple processes (expansion, compression, heat exchange, mixing, separation, chemical reactions, combustion of fuels) and analyses them using the exergy method. Examples of large thermal and chemical plant analysis are given in Chapter 5. Chapter 6 deals with the thermoeconomic applications of exergy, having as final scope the optimal *synthesis* of the complex systems.

This book is intended for under- and postgraduate students in mechanical and chemical engineering, for practicing engineers as well as for applied scientists concerned with energy conservation.

Ilie Siminiceanu

WALAS M. S., *Phase Equilibria in Chemical Engineering*. Butterworth Publishers, Boston, London, Sydney, 1985, XVI + 671 pp.

Most industrial processes in chemical-engineering are heterogeneous, involving gases, liquids, and solids. This book is devoted to the thermodynamic basis and practical aspects of the calculation of phase and chemical equilibria that are pertinent to such processes. The pattern of the book should be clear from the table of contents: 1. Equations of State; 2. Thermodynamic Functions and Equilibrium ; 3. Fugacity and Fugacity Coefficient; 4. Activity Coefficients; 5. Phase Diagrams ; 6. Vapor—Liquid Equilibrium ; 7. Liquid—Liquid Equilibria ; 8. Liquid—Solid Equilibrium ; 9. Other Topics ; 10. Chemical Equilibria ; 11. Evaluation of Changes in Enthalpy and Entrophy ; 12. Principles of Experimental Methods for Phase Equilibria. Besides the twelve chapters, this text includes : a list of figures, a list of tables, a list of examples, a preface, a guide for perplexed, eight appendixes (A to H), a substance index and a subject index. The references are presented in the appendix, grouped as collections of papers, books and individual papers. There are 216 figures and 112 tables in this text. The most important points are illustrated through solved numerical examples. In all, there are 139 examples and numerous computer programs written in BASIC as well as many problems designed for solution by the reader.

The reader may be a student in chemical engineering, a practicing engineer concerned with separation technology and process design, a scientist or a teacher of chemical engineering. The book is not only a practical guide for design ; it is a real encyclopedia and an academic treatise on phase equilibria in chemical engineering.

Phase Equilibrium in Chemical Engineering, as the other books of the Professor Stanley M. Walas, will certanly remain a fundamental work of chemical engineering sciences.

Ilie Siminiceanu

LEACH B. E. (Editor), *Applied Industrial Catalysis*. Vol. 3, Orlando 1984, XII+397 pp.

This last of three volumes has nine chapters. Each chapter was written by different industrial scientists, from U.S.A. and Italy, well known specialists in the field of catalysis theory and practice.

In Chapter 1, *Commercial Catalyst Preparation*, by N. Pernicone and F. Traina, the different unit operations generally used in catalyst manufacturing are described, with special emphasis on technological aspects. These „unit operations" are: precipitation and gel formation, filtration and washing, impregnation, coating, kneading, drying, calcination, grinding and sieving, dry mixing, tableting, extrusion, beading, leaching, melting and activation. Some typical examples of how such unit operations can be combined for the production of commercial catalysts are also given.

Chapter 2, *Oxyregeneration and Reclamation of Catalysts*, by R. E. Ellingham and J. Garrett, deals with the regeneration of the catalysts deactivated by coking, as well as with the reclaiming of the spent catalysts containing expensive metals, such as Mo, Co, Ni, V.

In Chapter 3, *Silica Gels: Preparation and Properties*, M. E. Winyall shows how the properties of both silica gel and precipitated silica are determined by the conditions under which the silica is gelled or precipitated, washed and dried. By varying these three steps, a large number of silicas, with different properties, can be obtained.

There are many catalyst applications that utilize alumina as a catalyst, carrier or bond. R. K. Oberlander describes how aluminas are made and how their preparation and treatment influence their properties, in Chapter 4: *Aluminas for Catalysts — Their Preparation and Properties*.

Chapter 5, *Ammonia Synthesis Catalysts in Industrial Practices*, by J. S. Merriam and K. Atwood, is a breaf history of the ammonia synthesis from the early work of Haber and Bosch to the present.

The homogeneous catalysis in liquid phase is an efficient way to control the selectivity of hydrocarbon oxidation. J. E. Lyons describes a number of these commercial reactions in Chapter 6, entitled *Catalytic Oxidation of Hydrocarbons in the Liquid Phase* (with 497 references !).

Olefin metathesis, originally termed olefin „disproportionation", discovered in 1959, opened up a new field of hydrocarbon chemistry. Current industrial applications of this reaction use heterogeneous catalysts based on molybdenum, tungsten and rhenium oxides supported on high-surface area alumina or silica. The development of processes and catalysts for olefin metathesis are treated in Chapter 7, *Olefin Metathesis: Technology and Application*, by L. Banks.

The use of catalysts for auto emission control became a fact in 1975, in U.S.A. and Japan, based on the research work started in 1958. In Chapter 8, *Catalysts and the Automobile — 25 Years Later*, W. Stanley Brigs traces the 25-year development of the catalysts and governamental regulations, ragarding HC, CO, and Nox automotive exhaust emissions.

Catalysis involving molecular sieve zeolites was reported in 1960. Since then molecular sieve zeolitic catalysts have found application in three main areas: refinery fuels processing, production of chemicals and environmental pollution control, Chapter 9, *Molecular Sieve Catalysts*, by W. Ward, is a review with 180 references on the characterization and industrial uses of zeolite catalysis.

This volume contributes to a better understanding of industrial catalysis and can be a valuable resource to all those concerned with catalyst invention theory and development.

Ilie Siminiceanu

DAVIDSON J. F., CLIFT R., HARRISON D., *Fluidization*; 2-nd edition, Academic Press, London, 1985, XIV+733 pp.

The first edition of *Fluidization*, edited by Davidson and Harrison, has been published by Academic Press in 1971. This new edition takes particular account of trends reported in the literature since 1971. On aspects of fluidiz-

ation there has been relatively little progress. On other topics there has been much progress and new chapters, regarding high velocity fluidization, granulation, combustion, have emerged. So, the new volume rather completes than replaces the old one. Similar to the old book, the new volume is compiled from chapters written by experts on different aspects of fluidization. When the titles remain the same as in the first edition (s. : Mixing, Elutriation, Spouted Beds, Drying, Heat Transfer), the authors are different. So, this second edition is realy a new book. Here are the twenty one chapters of the volume, and the contributors (in brackets) : 1. Incipient Fluidization and Particulate Systems (J.-P. Couderc — France) ; 2. Hydrodynamic Stability of Fluid-Particle Systems (R. Jackson — U.S.A.) ; 3. Continuous Bubbling and Slugging (R. Clift — England, J. R. Grace — Canada) : 4. Gaz Jets in Fluidized Beds (L. Massimilla — Italy) ; 5. Distributor Characteristics and Bed Properties (A. B. Whitehead — Australia) ; 6. Spouted Beds (J. Bridgwater — England) ; 7. High-Velocity Fluidization (J. Yerushalmi — Israel, A. Avidan — U.S.A.) ; 8. Downflow of Solids through Pipes and Valves (J. P. Jones — Netherlands, L. S. Leung — Australia) ; 9. Mixing (J. J. Van Deemter — Netherlands) ; 10. Fluidization of Dissimilar Materials (A. W. Nienow — England, T. Chiba — Japan) ; 11. Elutriation (D. Geldart — England) ; 12. Coare Particle Systems (T. J. Fitzgerald — U.S.A.) ; 13 A. Heat Transfer in Fluidized Beds : Convective Heat Transfer in Fluidized Beds (A. M. Xavier — Brasil, J. F. Davidson — England) ; 13 B. Heat Transfer in Fluidized Beds : Radiative Heat Transfer in Fluidized Beds (A. P. Baskakov — U. R. S. S.) ; 14. Immersed Tubes and Other Internals (O. Sitnai and A. B. Whitehead — Australia) ; 15. The Physical Behaviour of Three-Phase Fluidized Beds (R. C. Darton — Netherlands) ; 16. Drying (D. Reay and C. G. J. Baker — England) ; 17. Particle Growth and Coating in Cas-Fluidized Beds (A. W. Nienow and P. N. Rowe — England) ; 18. Chemical Reactors (W. P. M. Van Swaaij — Netherlands) ; 19. Fundamentals of Coal Combustion (R. D. La Nauze — Australia), Multiple-Spouted Gas-Fluidized Beds and Cyclic Fluidization : Operation and Stability (V. B. Kvasha — U.R.S.S.).

The book is intended for research workers, engineers working in industry as designers or managers of process plant, as well as for teachers of chemical engineering.

Ilie Siminiceanu

ANDERSON J. R., PRATT K. C., *Introduction to Characterization and Testing of Catalysts*. Academic Press, Sydney, 1985, IX+457 pp.

There are many methods and techniques for catalyst characterization and testing. The merit of this book is to present those types of measurement which are of dominant importance and, in author's experience, has given the best results for heterogeneous catalysts characterization.

The first chapter, *Surface Area Measurement*, deals with the total surface area, and with the measurement of the surface area of each chemical phase whick may be present in a complex solid catalyst (metal surface area, oxide surface area). The main adsorption measurement methods and apparatus are presented and illustrated by examples. Chapter 2, *Particle Size*, is a concise review of particle size reprezentation and estimation. The methods for the estimation of microparticles in a dispersed metallic catalyst, as well as the methods used for macroparticle size measurement of powders and granular solids are presented. Some of the suppliers of the equipment for many of the techniques described in this chapter are listed in Appendix 10.

In chapter 3, *Pore Structure*, the techniques for total pore volume, and for pore size distribution measurement are discussed. The authors recommend the most useful methods for each range of pore size : macropores (> 50 nm), mesopores (between 2 and 50 nm), and micropores (< 2 nm). Chapter 4, *Bulk Properties*, deals with an important class of properties, essential for the catalytic reactor design and operation. These are the densities, the mechanical properties (crushing, abrasion—atrition, and impact strenghth), and the thermal properties (thermal conductivity, thermal shock resistance).

In chapter 5, *Chemical Characterization,* emphasis is put on the most important surface chemical properties, namely : surface acidity and basicity. A special paragraph is concerned with the chemical characterization of bimetallic catalysts.

Chapter 6, *Testing of Catalysts Activity,* deals with the most important properties of catalysts : catalytic activity, selectivity, and life. The main types of laboratory scale reactors, as well as the peripheral equipment, are discussed. Some other practical subjects, i.e. standardization of catalyst activity testing methods, and even laboratory safety, are also outlined. The authors consider that the precise kinetic data now available from laboratory-scale experimentation, the improved mathematical models, and the advances in digital computation techniques allow the design of commercial reactors on the basis of banch scale results. So the pilot plant should be a scale-down version of the projected commercial plant, used primarily to confirm the design calculations rather than for design data generation, as in the traditional strategy.

The purpose of the last chapter (Chapter 7 : *Physical Instrumental Methods)* is to describe the physical instrumental methods which can be used to reveal the individual phases of the complex catalysts, their surface composition and structure. These are : electron microscopy (TEM, SEM, STEM,...), electron spectroscopy, X-ray emission and absorption, ion beam methods, M ö s s b a u e r spectroscopy, magnetic resonance, spectroscopy (NMR, ESR), vibration spectroscopy, UV-visible diffuse reflectance spectroscopy, photoacustic spectroscopy (PAS).

Each chapter ends with references and with literature classified by topic. The basic text, the examples given in almost every chapter, and the appendixes with various numerical data make this book a real practical guide for those working in the research, design and development of heterogeneous catalytic processes.

Ilie Siminiceanu

SCRIBAN RENÉ (coordonnateur), ARBAUD ALAIN, BENARD MAX, BERSET CLAUDETTE, BOCQUET JOËLLE, BOUIX MARIELLE, DE ROSNAY JOËL, DUBUIS THIERRY, GALZY PIERRE, GOURSAUD JEAN, GUIRAUD JOSEPH-PIERRE, KUBIAK CATHERINE, LARRIEU JEAN, LEVEAU JEAN-YVES, POURQUIE JAQUES, RICHARD HUBERT, VANDECASTEELE JEAN-PAUL, *Biotechnologie. 2-e éd.,* Technique et Documentation Lavoisier, Paris, 1984, 688 p.p.

Cet ouvrage didactique a tenté d'évoquer ce que sont et ce que pouront devenir les biotechnologies dans notre monde des prochaines décades.

Ce livre, dans toutes ses sections — Historique, Le génie microbiologique, Le génie enzymatique. Le génie génétique, Le controle qualité en biotechnologie sur les matières premières en cours et les produits finis, La biotechnologie en France et dans le monde — a tenté de compléter les textes de syntièse par une bibliographie exhaustive. Cette dernière permettra à chacun, selon sa formation ou en fonction du problème qui l'intéresse, d'avancer en profondeur dans la connaissance de telle ou telle question posée par les industriels à la recherche d'améliorations ou d'innovations en bioindustrie.

Pour la deuxième édition de ce volume de référence, les auteurs ont tenu compte des derniers progrès des différentes techniques composant la biotechnologie. Toutes les parties ont été revues et mises à jour. Certaines parties ont été développées (physiologie des microorganismes) et le chapitre concernant la valorisation des déchets et effluents a été considérablement augmenté. Un chapitre sur la „conversion de composés ligno-cellulosiques" a été ajouté et „les perspectives d'avenir" ont été réactualisées.

Severian Dumitriu

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